THE CHEMICAL AND PHYSICAL ANALYSES OF NEW AND DEGRADED LUBRICATING OILS

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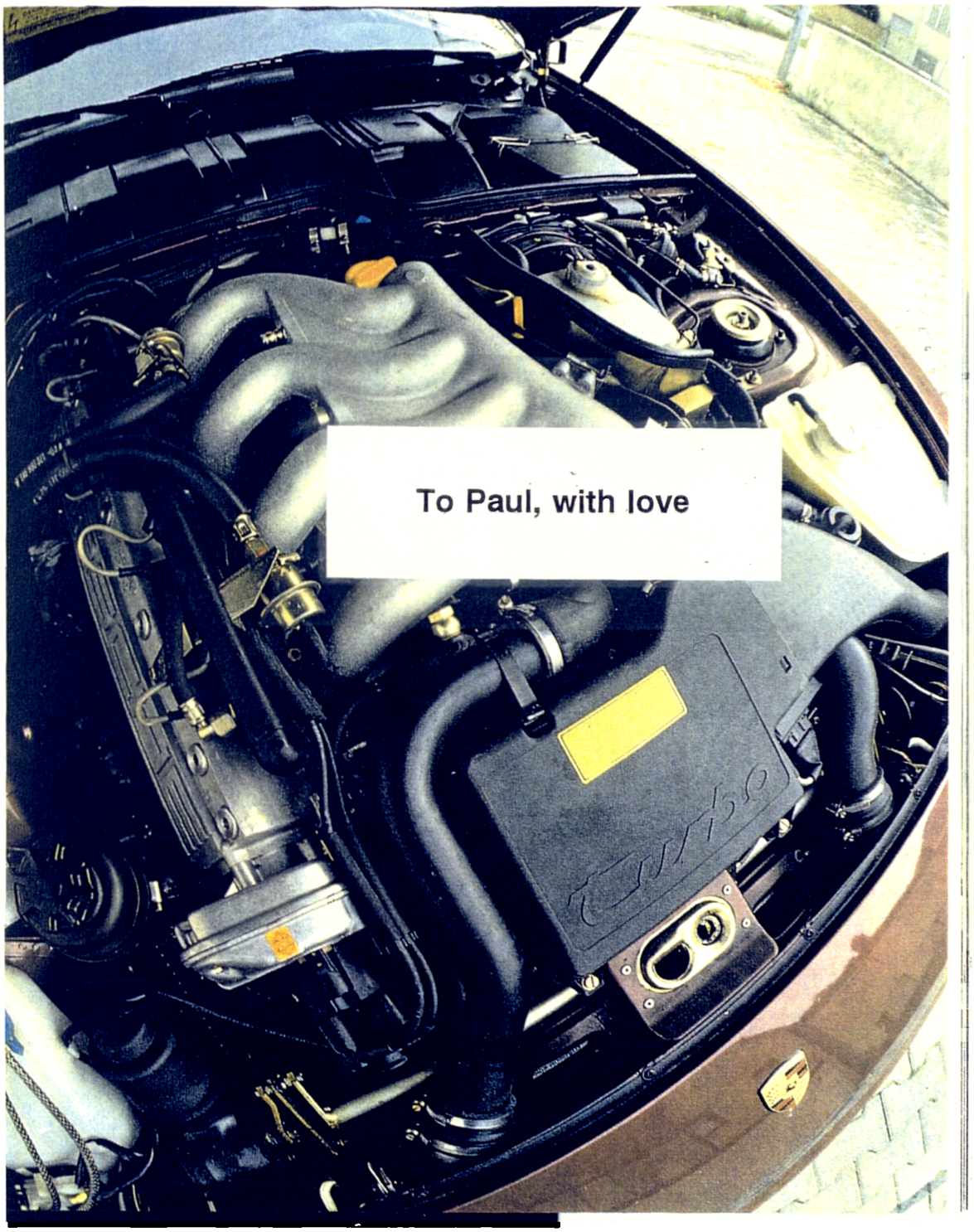
To Paul, with love

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Abstract

Petroleum based lubricating oils have been widely used since the middle of the 19th century. Automotive lubricants are designed to function under the severe operating conditions of modern high performance combustion engines. Engine tests have been developed over the years to classify lubricants according to their performance in various engines. These tests are both expensive and time consuming, resulting in the development of screening tests. Screening tests are frequently used, typically small scale laboratory or engine tests that are cheap to run and can be carried out at a high rate. A novel test method was developed at De Montfort University known as 'Top Ring Zone Sampling', where oil is sampled from the ring zone of an operating test engine.

The project aim was to characterise top ring zone samples, together with fresh and other used oils, according to their chemical and physical properties. Due to the small amount of ring zone sample collected, typically 1g/hour, previous workers have analysed the oils using infrared spectroscopy and non-aqueous conductimetric titration methods. Additional techniques were required to analyse the samples in more detail. The main objectives were to modify a Four Ball Tester enabling the analysis of top ring zone oils, to develop a thermogravimetric method to determine the volatility characteristics, to develop methods of separation and finally to find a suitable method for the interpretation of the results.

The first two objectives were successfully accomplished followed by the development of a dialysis method for examining the degree of degradation in both gasoline and diesel used oils. By dialysing the oil samples the oxidation products were isolated from the high molecular weight additives and soot contaminants. Although such a method has been used before to separate additives and fresh oils, the method had not previously been applied to top ring zone samples, which contain a very high particulate content in the case of diesel samples. A technique known as principal component analysis was used to

interpret the results obtained, successfully comparing the oil samples based on all the results simultaneously. The top ring zone samples were unique due to their low volatility and apparent negligible oxidation.

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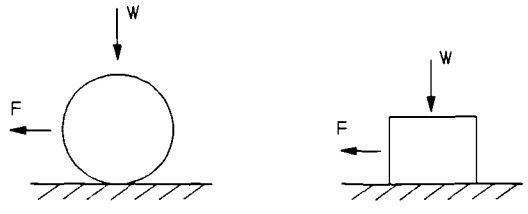
CHAPTER 1 Introduction

The movement of one solid surface relative to another is fundamentally important to the function of many kinds of mechanism. The science and technology of interacting surfaces in relative motion, otherwise known as "tribology", embraces the study of friction, wear and lubrication. **Friction** is mechanical resistance to the relative movement of two surfaces. Whenever two surfaces pass over each other **wear** will occur, with damage to one or both surfaces, generally involving the progressive loss of material. The reduction of friction, and often wear, can be accomplished by the introduction of a **lubricant**. Hence the study of lubrication is closely related to the study of friction and wear.

1.1 Friction

All solid surfaces are uneven if examined on a sufficiently small scale. When two nominally plane and parallel surfaces are brought together contact only occurs between the high spots, or asperities. Points of contact are responsible for supporting the load and generating any frictional forces. These forces arise from an adhesive force developed at the areas of contact and a deformation force required to plough the asperities of the harder surface through the softer. In the diagram below, the force required to cause motion, either by rolling or sliding of one surface over another is labelled F. The ratio between this frictional force F and the normal load W is known as the coefficient of friction, and usually denoted by the symbol μ:



where

$$\mu \leq \frac{F}{W}$$

Figure 1.a

One way to reduce the frictional force, and often wear, is to introduce a lubricant.

1.2 Lubrication

A lubricant provides a layer of material whose shear strength is lower than that of the moving surfaces. The lubricant may not completely prevent asperity contact, although it will reduce it and may also reduce the strengths of the asperity junctions formed. A variety of materials, gases, liquids or solids may be used as lubricants. The types of lubrication provided are:

hydrodynamic - surfaces are separated by fluid film, which is relatively thick when compared to asperities.

elastohydrodynamic - occurs when local pressures are so high and lubricant film so thin that elastic deformation of surfaces occurs.

boundary - surfaces are separated by a solid interfacial film of low shear strength.

solid lubricants - provide a solid interfacial film of low shear strength.

One of the most common lubricants is oil, the most important property of which is its viscosity, a measure of its internal friction or reluctance to shear.

1.3 Viscosity

The absolute viscosity of a liquid has been defined as the relationship between the shear stress τ and the shear rate S by Newton.

$$\tau = \eta \times S$$

where η is the absolute viscosity. The unit of absolute or dynamic viscosity is the Pascal-second Pas, the more common unit being the Centipoise ($1cP=10^{-3}Pas$). Another common expression of viscosity is kinematic viscosity which is given by;

$$\nu = \frac{\eta}{d}$$

where d=density. The unit of kinematic viscosity is m^2s^{-1}, and the commonly known unit is the Centistoke ($1cSt=10^{-6}m^2s^{-1}$).

Viscosities are usually determined at more than one temperature because it is important to know the viscosity characteristics of an oil over a range of temperatures. All lubricants become thinner (lower in viscosity) as the temperature is increased but the viscosity decrease can vary significantly depending on the type of oil. An empirical scale known as the viscosity index (VI) has been devised to indicate the effect of change of temperature on the viscosity of an oil. The higher the VI the less the effect of temperature on the viscosity of the oil. The VI of an oil is calculated from kinematic viscosity measurements determined at 40°C and 100°C. The equation used for the calculation of VI for the range 0 to 100 is given below.

$$VI = \frac{L-U}{L-H} \times 100$$

where

U = kinematic viscosity at 40°C of the oil whose VI is to be calculated

L = kinematic viscosity at 40°C of an oil of 0 VI having the same kinematic viscosity at 100°C as the sample under test

H = kinematic viscosity at 40°C of an oil of 100 VI having the same kinematic viscosity at 100°C as the sample under test

L and H are obtained from standard tables.

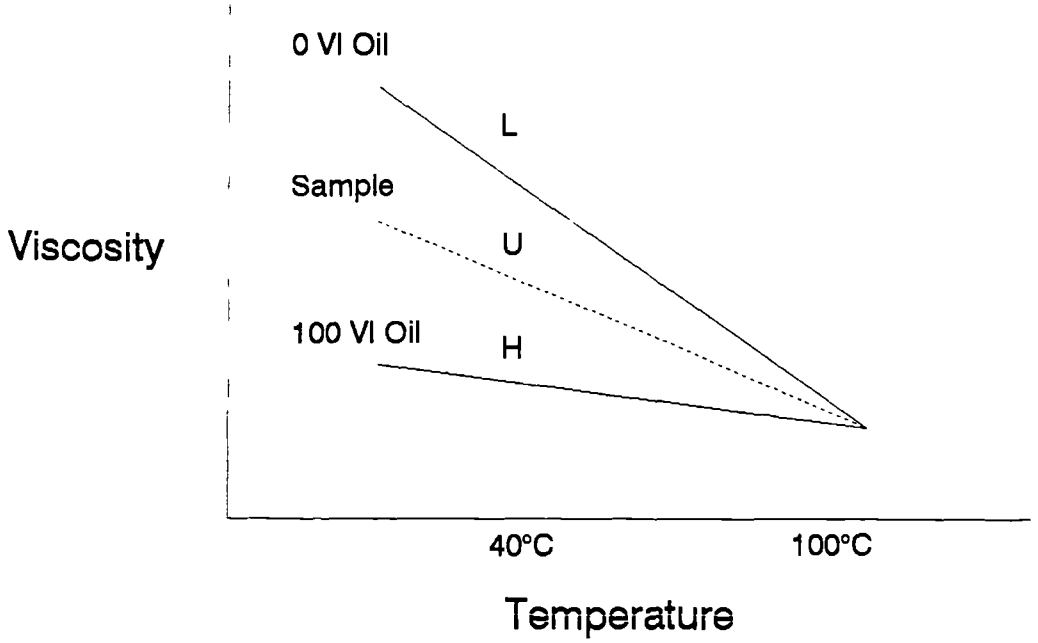


Figure 1.b

A modified procedure applies to oils of VI above 100 (eg synthetic oils) or to oils of high viscosity.

1.4 Lubricating Oils

Naturally occurring oils, those of mineral, vegetable, animal or fish origin had been quite satisfactorily used up until the Industrial Revolution. During the latter part of the 19th century the demand for lubricants increased, primarily due to the introduction of the reciprocating engine. The first petrol engine was invented in 1886 by Karl Benz and Gottlieb Daimler. Shortly after, in 1890, a British engineer Herbert Ackroyd-Stuart patented the fundamental features of the compression

ignition engine. In 1892 a German engineer Rudolph Diesel took out a patent, claiming the invention of the "Diesel" engine. The demand for combustion engine lubricants coupled with the increase in demand for vegetable and animal oils led to the adoption of mineral oils for engine lubrication.

The earliest well drilled specifically for oil is credited to 'Colonel' Drake of the Seneca Oil Company. The well was drilled in 1859 at Titusville, Pennsylvania and marks the birth of the petroleum industry. Engine lubricating oils are manufactured by blending additives into base oils, which are normally obtained from petroleum.

1.5 Base Oils

Crude oil is of little use prior to the refining process. It is a complex mixture of gases, liquids and solids, all of which are hydrocarbons. Small impurities are present principally as sulphur-, nitrogen-, oxygen- and chlorine- containing compounds. Crude is distilled into useful products such as gas, gasoline, kerosine, diesel, lubricating oils, wax etc.

Base oils are produced from the atmospheric residue of the crude oil distillation. The residue is distilled under reduced pressure to give base oil fractions of varying boiling ranges. Each fraction varies in viscosity ranging from a thin (low viscosity) spindle oil to a thick (high viscosity) brightstock. The base oil fractions are further refined to improve their chemical and physical properties. The processes involved usually include:

solvent refining - improves oxidative stability and viscosity/temperature properties.

solvent dewaxing - removes wax at low temperature.

finishing process - improves colour, odour and removes remaining impurities.

The finished base oils are then used in the manufacture of lubricating oils.

1.6 Oil Additives

Base oils alone are not capable of performing the functions required of an engine lubricant which in the long term include:

1) minimisation of friction
2) minimisation of wear
3) cooling the running parts
4) provision of a good seal in the piston ring zone
5) removal of debris from top ring zone
6) keep engine clean internally
7) resistance to degradation of oil itself
8) prevention of internal corrosion

An engine lubricating oil is manufactured by blending additives into a base oil to meet the requirements listed. These additives are often multifunctional but can be described in general terms.

1.6.1 Detergent-Dispersant Additives

These additives help to prevent deposition of lacquer films and carbon deposits on the sides of the pistons and on the piston rings and grooves, which are subject to very high temperatures as well as accumulations of solid combustion products. They also help to keep metal surfaces free of carbon and the rings free in their grooves. In addition, they maintain the soot and lead particles finely dispersed in the oil. Detergent types include sulphonates, phenates, salicylates,

phosphonates, and dispersant types include alkylsuccinimides, Mannich bases and succinate esters.

1.6.2 Oxidative Inhibitors

These enhance the natural oxidation resistance of the lubricant and delay the formation of gums or varnishes which largely contribute to ring sticking in engines operating under prolonged high temperature conditions. The oxidation process is controlled by the decomposition of the peroxide radicals, or by terminating free radical reactions. Typical additives include zinc dialkyldithiophosphates (ZDDP), hindered phenols or aromatic amines.

1.6.3 Corrosion Inhibitors

The water produced during the combustion process does not always pass harmlessly out of the exhaust pipe as steam, particularly under cold running conditions. The metal surfaces are very prone to rusting due to the effects of this water, which also contains acid from the combustion products. The corrosion inhibitors provide a film of protection on the surface of the metal. Agents available include ZDDP, metal sulphonates, fatty acids and amines.

1.6.4 Viscosity Index Improvers

The viscosity index (VI) is a measure of the variation of viscosity with temperature, as described earlier. A low viscosity index indicates that the viscosity rapidly decreases with an increase in temperature. Certain long chain polymers increase the VI by increasing the viscosity at high temperatures. Examples include polymethacrylates (PMA) and olefin coploymers (OCP). However, some hydrocarbons have naturally high VI values and are known as XHVI oils. A multigrade oil can be formulated using a XHVI oil without a polymeric VII.

1.6.5 Pour Point Depressants

These substances prevent crystallisation of wax at low temperatures, ie lowering the temperature at which the oil pours. Additives include polymethacrylates or alkylated naphthalenes.

1.6.6 Anti-wear and EP (extreme pressure) Agents

These reduce the friction between moving parts and prevent scoring and seizure. Agents employed for this purpose include ZDDP, organic phosphates and organic sulphur compounds. This illustrates the multifunctional nature of most additives.

The type and proportions of additives depend upon the type of lubrication required. Diesel fuels contain more sulphur than gasoline and therefore produce more corrosive gases when burned. Diesel engines usually run at higher power loadings than gasoline engines and are therefore more likely to form high temperature deposits. Diesel lubricants are therefore formulated with emphasis on the anti-oxidant and dispersant/detergent type additives.

1.7 SAE Viscosity Classification

As the demand for more sophisticated lubricants has increased, so too has the number of different types of base oils and additives. Consequently, fully formulated oils can vary considerably according to both their chemical and physical characteristics. A method was required for distinguishing between the many types of lubricating oils. A simple classification of oils, the SAE (Society of Automotive Engineers) numbering system, was introduced in the 1920's, based purely on viscosity measurements, when it became obvious that expressions such as Super, Heavy Duty, Summer and Medium were too vague. First, the SAE established four narrow ranges of viscosity and gave them the numbers

SAE 20 (lightest), 30, 40, 50, covering the span of viscosities in use. Later the series was extended to include even lighter oils, originally specified at 0° F and each was given the suffix W, for winter. These were designated the SAE numbers 5W, 10W and 20W. Further grades were added, 0W, 15W and 25W, to satisfy the ever-increasing precise requirements of modern engines. The current list is given in Table 1.a.

Table 1.a

SAE Grade	Low-Temperature (°C) Cranking Viscosity, cp Max	Low-Temperature (°C) Pumping Viscosity, cp Max With No Yield Stress	Kinematic Viscosity (cSt) at 100°C Min	Max	High-Shear Viscosity (cp) at 150°C 10^6 s^{-1} Min	
0W	3250 at -30	30 000 at -35	3.8	--	--	
5W	3500 at -25	30 000 at -30	3.8	--	--	
10W	3500 at -20	30 000 at -25	4.1	--	--	
15W	3500 at -15	30 000 at -20	5.6	--	--	
20W	4500 at -10	30 000 at -15	5.6	--	--	
25W	6000 at -5	30 000 at -10	9.3	--	--	
20	--	--	5.6	<9.3	2.6	
30	--	--	9.3	<12.5	2.9	
40	--	--	12.5	<16.3	2.9	(0W-40,5W-40, and 10W-40 grades)
40	--	--	12.5	<16.3	3.7	(15W-40,20W-40,25W-40, 40 grades)
50	--	--	16.3	<21.9	3.7	
60	--	--	21.9	<26.1	3.7	

A multigrade oil is classified by two numbers, eg 10W-40. The number before the hyphen represents the viscosity at low operating temperatures, and that after the hyphen is the high-temperature viscosity. The grade designated to an oil gives no indication of its quality, only its viscosity properties. The quality of an oil can be evaluated either by the determination of some physical or chemical property

such as viscosity, volatility, sulphur content in a laboratory or by its performance characteristics eg engine test.

1.8 Test Methods

Many of the test methods used in the petroleum industry for quality control have been standardised by the Institute of Petroleum (IP) or by the American Society for Testing and Materials (ASTM), or both as a jointly accepted method. Various national standardising bodies in different countries have also adopted many of the same methods. The British Standards Institution (BSI), which has produced the BS2000 series of standard tests for petroleum and its products, have adopted selected IP methods. The ASTM and IP have contributed significantly to the production of internationally accepted methods, as specified by the International Standards Organisation (ISO). Some of the most common test methods carried out include the determination of:

1. Viscosity
2. Viscosity Index
3. Pour Point
4. Flash Point
5. Density
6. Oxidative Stability

The test methods are continually updated and new ones developed. For example the Institute of Petroleum thermal analysis panel (STG-9) discuss methods such as wax appearance temperature by DSC, volatility by TG and oxidative stability by PDSC.

No single laboratory test can predict the performance of an oil in an engine, although a series of different tests may indicate an oil's suitability in a particular application. Ultimately the only way to adequately determine the performance of

an oil is to test it under real operating conditions, ie, in the engine it is to be expected to lubricate. This can be very expensive and time consuming. Oil companies and large users of oil, for example government departments and research establishments, have established engine test procedures.

1.9 Engine Tests

Engine tests are designed to assess or rate lubricating oils on the basis of one or more of the following as primary considerations:

Lacquer formation	Bearing corrosion
Sludge formation	Wear
Ring sticking	Engine cleanliness

The general procedure is to select an oil which has given complete satisfaction in service and test this in the test engine to establish a basis of comparison. Such an oil is a "reference" oil. New oils are then run in the same engine under exactly the same conditions and the results, eg. piston deposits, of the test are compared with those obtained by the reference oil. Many different engine tests are used for the classification of oils, based on the performance of the oil under test.

1.10 Classification of Lubricants

A recent article published in Petroleum Review [1] describes the classification of lubricants and is summarised below.

United States - 'Tripartite

By far the most influential of all organisations to define and develop automotive crankcase lubricant qualities in the world has been the 'Tripartite' collaboration

of the three large American organisations - SAE, ASTM and API.

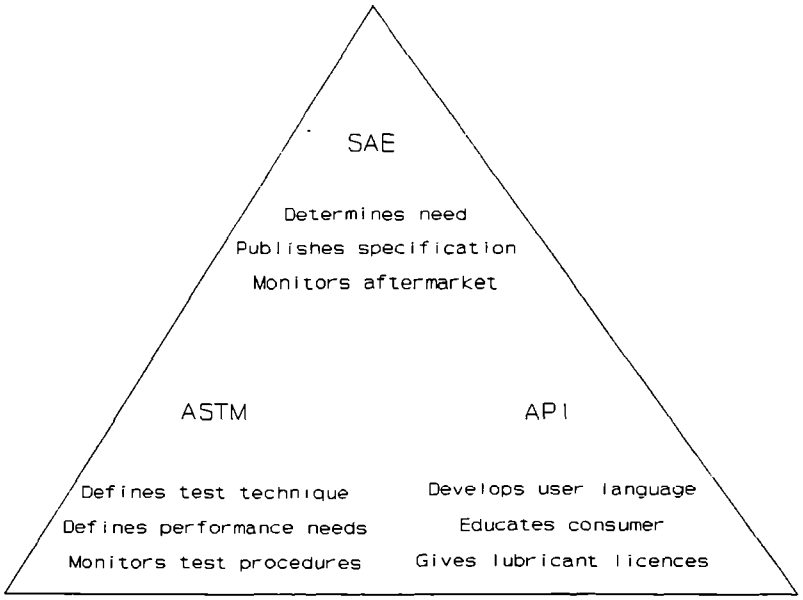


Figure 1.c

In the early 1950's, the American Petroleum Institute (API) introduced a system for classifying the various types of service conditions under which engines operate. These were designated as ML, MM, MS (for gasoline petrol engines) and DG, DM, DS (for diesel engines) but no performance standards were specified. In 1969-70 API, in cooperation with the American Society for Testing and Materials (ASTM) and the Society of Automotive Engineers (SAE) established a new engine service classification for engine oils. ASTM defined test methods and performance targets, API developed the service letter designations and 'user language', and SAE combined the information into an SAE recommended practice in the SAE handbook for the consumer. The current revision of that report is 'Engine Oil Performance and Engine Classification' - SAE J 183 JUN 91.

The current API Engine Service Classification is divided into an 'S' series, those oils sold in service stations, mainly for petrol engines, and a 'C' series, for commercial oils, mainly for diesel engines. An oil can meet more than one classification eg API SG/CD. The API SG category was adopted in March 1988, meeting the requirements of 1989 passenger cars. The API CE was also adopted in 1988 and recommended by all-American heavy duty engine manufacturers. In 1990 it was replaced by API CF-4 for four stoke engines. Plans to issue an API SH classification this year are well advanced. Before an oil can be allocated any given API performance level, it must satisfy requirements laid down for various engine tests.

Manufacturers Specifications

Vehicle manufacturers also issue their own specifications to cater for the special operating characteristics of the engines they produce. The need for individual specifications in the last few years has reduced because of the existence of CCMC classifications.

Europe - CCMC

The Committee of Common Market Automobile Manufacturers (CCMC) was a trade association founded in 1972, lasting until late 1990. In 1991 it was replaced by a differently structured organisation ACEA (Association des Constructeurs Europeens d'Automobiles). The fuels and lubricants working group within CCMC first published their classifications or 'sequences' in 1975. These covered additional requirements over and above the API designations, due to the needs of the European market. The classifications were extensively revised in 1984 and 1991. The latest sequences include:

G-4 minimum quality for passenger car gasoline engines.
G-5 low viscosity fuel economy oil for passenger car gasoline engines.

PD-2 for passenger car diesel engines.

D-4 minimum quality for commercial vehicle diesel engines.

D-5 as D-4 but for more severe service or extended drain.

Performance parameters such as high temperature, high shear viscosity and **volatility** were recognised widely for the first time. CCMC classifications were based mainly on CEC test procedures. CCMC has never given approvals, due to the financial costs of developing and maintaining the necessary bureaucracy.

Europe - CEC

In Europe the Coordinating European Council for the Development of Performance Tests for Transportation Fuels, Lubricants and Other Fluids (CEC) has a parallel but more limited role than ASTM in the United States. Its scope is limited to performance tests (essentially engine and rig tests) and although it develops tests no limits are set on the tests, that is the responsibility of the commercial organisations. Many of the lubricant engine tests are less rigorously defined than their US counterparts. The CEC is working with ACEA, ATIEL (Association Technique de l'Industrie Europeene des Lubrifiants) and ATC (Technical Committee of Petroleum Additive Manufacturers in Europe) to develop a way to modernise its practices.

Japanese activities

The Japanese manufacturers have generally relied on the API classification system. The Japanese Automobile Standards Organisation (JASO) has developed four engine test procedures without giving pass/fail limits, similar to the CEC. The tests are not required, however, in or outside of Japan by the vehicle manufacturers to meet their own specifications. Since 1990 the Japan Automobile Manufacturers Association (JAMA) has worked with the Motor Vehicle Manufactures Association of the United states (MVMA) to develop a new

performance standard called ILSAC (International Lubricants Standardisation and Approval Committee). The aim is to have worldwide lubricant specifications.

1.11 Screening Tests

Before an oil reaches the market it can therefore undergo a vast number of engine tests to meet the requirements of the many different organisations, as mentioned above. This is obviously expensive and time consuming.

When developing a new automotive lubricant, engine tests are not always suitable due to the cost and time required. Screening tests are frequently used, typically small scale laboratory or engine tests that are cheap to run and can be carried out at a high rate either by being short in duration or by being easy to complete in large numbers. If screening tests can be correlated with engine test performance then vast savings can be made in terms of cost and time.

1.12 Top Ring Zone Sampling

Oil which comes into contact with the severe operating conditions of an engine, around the piston zone, is destined to be both chemically and physically degraded. The oil is subjected to extreme temperatures and pressures, as well as intimate contact with highly reactive combustion gases. Oil which is transported to this region can either be lost amongst the exhaust gases or returned to the sump. Degradation of the sump oil can be attributed to the accumulation of the degraded oil from the piston region. Collection of this degraded oil prior to its return to the sump is appealing as the condition of the oil assessed within a few hours can reflect the condition of the sump oil after many hours. If the performance of an oil in an engine test can be correlated to the condition of the ring zone oil after a few hours, then this type of sampling would lead to the perfect screening test.

Work reported by Richard [2] describes the collection of samples directly from the piston zone of operating engines. A 1.0mm hole was placed in the liner at a position such that it was bisected by the top face of the upper ring at Top Dead Centre (TDC). This led through the liner and cylinder block to the outside of the engine where a 0.3mm diameter control jet limited the gas flow to a value close to the normal blow-by past the piston. The oil mist was extracted from the evolved gas using a simple separator consisting of steel balls, and collected into a weighed sample bottle. The sample weighed between 2-4g per hour. Blockages were easily rectified by changing the control valve outside the engine. A series of 50hr runs were made under CEC conditions and the samples analysed for additive content, viscosity, volatility and oxidation. Results obtained for a Petter AVB supercharged diesel engine showed considerable loss of volatility, increase in viscosity and neglible oxidation, as measured by the IR absorbance at 1710cm^{-1}. Comparison of results obtained from a Caterpillar engine suggested that the air/fuel ratio has a strong influence on both oxidative degradation and degree of thickening, as oil from the ring zone of the Caterpillar did show significant oxidation and increased thickening.

A technique developed at De Montfort University, then Leicester Polytechnic, allowed samples to be obtained from any position within the ring pack, using an **internal** sampling system. Work carried out, in collaboration with Shell is described by Saville et al [3]. The sampling system used on two engines was basically the same. A 1.0mm diameter hole was drilled from the top ring groove on the anti thrust face of the piston to a small fitting (min internal orifice 0.5mm) in the piston crown. A length of PTFE tubing passed from the piston undercrown down the con rod, and out of the side of the crankcase. Small samples were collected, approximately 1g per hour. Initially studies were carried out using a Petter AA1 diesel engine at De Montfort University. Later further studies were made on a Caterpillar diesel engine at Shell Research Centre, where the majority of the analyses were carried out using well established techniques, including infra-red analysis, Base Number determination, pressurised differential scanning

calorimetry (PDSC), thermal gravimetry (TG), gas chromatography (GC), viscosity measurements and nuclear magnetic resonance (NMR). Samples obtained from the top ring groove (TRG) of the Petter AA1 showed loss of volatility, fuel dilution and oil oxidation (determined by absorbance at 1710cm^{-1} and by an isothermal PDSC method). Results from the analysis of Caterpillar TRG samples showed viscosity increase, no fuel dilution, loss of volatility, increase in soot levels and oxidation.

In 1990 Thompson and Saville [4] reported ring zone sampling studies carried out in their laboratories to investigate oil consumption mechanisms. The sampling system was an improved version of that previously described by Saville et al [3] where the flexible tube was unsupported and suffered mechanical failure after a relatively short time (<24 hours). The improved system includes a two-bar linkage, attached to the big-end and a fixed point outside the crankcase, to support the sampling pipe. The durability of the system was extended to over 100 hours. The additive content, viscosity and volatility of the oils were determined, showing loss of base oil in top ring groove samples. No measure of oxidation was reported.

In 1991 Bush et al [5], De Montfort University, reported a program of work based on the top ring zone sampling from a Villiers C-30 air-cooled, spark ignition engine running on natural gas. The method adopted was that of Richard [2], through the bore wall. The samples collected were analysed showing a decrease in Base Number, increase in Acid Number, loss of base oil, loss of oxidative stability as determined by PDSC, no apparent oxidation as determined by infra-red analysis and loss of VII.

Unpublished work completed at De Montfort University since the Shell collaborative work includes the continuation of internal sampling from the Petter AA1 diesel engine (sponsored by BP) and the internal sampling from a Petter W1 gasoline engine, (sponsored by Castrol). Analyses at De Montfort University were

limited to the determination of Base and Acid numbers by conductimetric method and infra-red analysis of the neat sample. The sampling time varied according to the life time of the PTFE tubing. The Petter W1 generally ran for approximately 5 hours and the Petter AA1 up to 10 hours. Current projects include the sampling from the Petter AA1, sponsored by Kuwait Petroleum and the internal sampling from a Caterpillar engine, sponsored by Caterpillar.

1.13 Aims and Objectives of the Project

The aim of this work was to characterise oil samples obtained from the top ring zone of an operating combustion engine according to their chemical and physical properties. Due to the small amount of oil sample collected, typically 1g/hour, previous research workers have analysed the samples using infrared spectroscopy and non-aqueous conductimetric titration methods. Additional techniques were therefore required to assess these unique samples in more detail. The main objectives were to;

1. To modify a Four Ball Tester enabling the testing of top ring zone samples.

2. Develop a thermogravimetric method for the determination of automotive oil volatility.

3. Develop techniques for the separation of fresh and used oils, primarily to isolate the degradation products.

4. Finally, having established a set of analyses a statistical method of data analysis was required for the interpretation of the results obtained.

CHAPTER 2 Volatility by TGA

2.1 Background

The development of fuel-saving automotive engine oils has become an important concern in recent years in connection with the need to reduce CO_2 emissions, a major cause of global warming. The tendency to use thinner oils has therefore increased, reducing internal friction and hence fuel consumption. As multigrade automotive oils are expected to function both at low and high operating engine temperatures, volatile components will evaporate to some extent at the higher operating conditions. This will result in an increase in oil consumption, an increase in viscosity and a decrease in both low temperature performance and fuel efficiency. Loss of oil due to volatility is therefore of great importance. This is reflected by the more stringent test procedures specified by the Comité des Constructeurs d'Automobiles du Marché Commun (CCMC), now ACEA, including volatility specifications. Standard published methods for the determination of volatility characteristics include simulated distillation (ASTM 2887), 22 hour evaporation (ASTM 972) and a 1 hour evaporation, the Noack Test (DIN 51581). Thermogravimetric analysis has also been used, although a standard method has not yet been adopted industrially.

Viscosity and volatility characteristics of engine oils have been reported by Davis [6,7], where a thermogravimetric (TG) method was used to compare the volatilities. A 10-12mg sample was heated at 10°C/min in a platinum pan in a nitrogen atmosphere until no further evaporation was observed. The different oils were compared by examination of the thermogravimetric traces. In 1987 Didcot et al [8] correlated volatility and kinematic viscosity with oil consumption, where the volatility measurements were determined by method ASTM 2887. Zinbo and Skewes [9] described a TG method in 1989 for engine oil volatility and correlated the results with those obtained by the Noack Test. A 12-14mg sample was heated in an aluminium pan at 25°C/min to an isothermal temperature and then

kept at this temperature for ≈35 minutes, under constant air flow. Using these conditions the time taken to obtain a 30% evaporation weight loss for tetracosane was determined, $t_{tetracosane}$. The relative evaporative weight loss of an oil sample was then taken as the weight loss after time $t_{tetracosane}$. In 1990 a study of low-viscosity oils was reported [10], where the fuel consumption, oil volatility and engine wear were determined. A relationship between oil consumption in an engine and volatility as determined by the Noack test was developed, showing that 17% was the upper limit for the Noack evaporation loss to assure an acceptable level of oil consumption for the ordinary fuel saving oils. In 1991 Gustavsson [11] reported a TG method which correlated Noack and TG results. In summary 50µl oil samples were heated from 50°C to 250°C at 40°C/min in a Mettler aluminium oxide pan, in a nitrogen atmosphere, to give a % weight loss over 15 minutes. It was also shown that small changes in the analysing temperature have considerable impact on the weight loss whereas a small decrease in purge gas did not change the results significantly.

The thermal analysis panel at the Institute of Petroleum (IP) developed a TG method for volatility measurements based on a temperature ramped program, initial work was reported in 1985 [12]. The proposed method as given in Petroanalysis '87 [13], was as follows: oil heated at 10°C/min from 40°C-550°C under nitrogen. The % weight loss as a function of temperature was reported. Satisfactory repeatability was achieved, but reproducibility was poor primarily due to temperature calibration and pan geometry. This method was first published as a proposed method (PM-BC) in the 1988 edition of the IP "Standard Methods for Analysis and Testing of Petroleum and Related Products".

A new method is currently being developed by the IP panel based on the method described by Zinbo and Skewes [9]. This method does not require a temperature calibration as the results are relative to a standard. It was also hoped that the reproducibility of the method would be acceptable. The relative volatility results are to be correlated with those obtained by the Noack method.

2.2 IP Draft Method

In summary, a small sample (10mg) of oil is held at a fixed temperature in a thermogravimetric analyser to determine the mass loss over 30 minutes. The relative volatility is calculated as the mass loss of the oil divided by the mass loss of the reference material squalane (2,6,10,15,19,23-hexamethyltetracosane).

2.2.1 Selection of Suitable Isothermal Temperature

A suitable isothermal temperature is one which gives a mass loss of 1.6 ± 0.2 mg over 30 minutes for 10.0 ± 0.5 mg squalane. To determine this, 10mg ± 0.5 mg squalane is heated at 20°C/min to 180°C, then at 1°C/min to 210°C. Inspection of the mass versus temperature plot gives the temperature at which the rate of mass loss is between 0.045 and 0.06 mg over 1°C, which is equivalent to 1.4 to 1.8 mg over 30 minutes. This is the isothermal temperature.

2.2.2 Procedure

A 10.0 ± 0.5 mg sample is heated in an aluminium flat based cylindrical pan from 50°C at 10°C/min to an isothermal temperature, in a nitrogen atmosphere, and held for 30 minutes, taking time=0 as the time when the isothermal temperature was first attained. Squalane is initially run in duplicate, ensuring that the mass loss over 30 minutes does not vary by more than 0.1mg.

2.2.3 Calculation

From the mass vs time curve, the mass loss m_{sample}, of the sample over the 30 minute period t=0 to t=30 minutes to the nearest 0.01mg is recorded. The average mass loss for repeated runs of squalane is denoted $m_{reference}$.

$$\textbf{Relative Volatility} = m_{sample} / m_{reference}$$

2.2.4 IP Draft Method Results

Initial results were obtained using a Stanton Redcroft TG-750 Thermal Analyser. Unlike modern instruments it could not automatically switch from heating at 10°C/min to holding a fixed temperature with the accuracy required for the IP draft method. The milli-volt signal from the furnace thermocouple was therefore continually monitored using an accurate digital volt meter such that the instrument could be manually switched to the 'hold' setting once the voltage corresponding to a particular temperature had been reached. Using a platinum pan designed for the instrument (aluminium pans not being available) the mass and temperature for each sample run were continuously recorded using a paper chart recorder. A typical trace is shown in Figure 2.a.

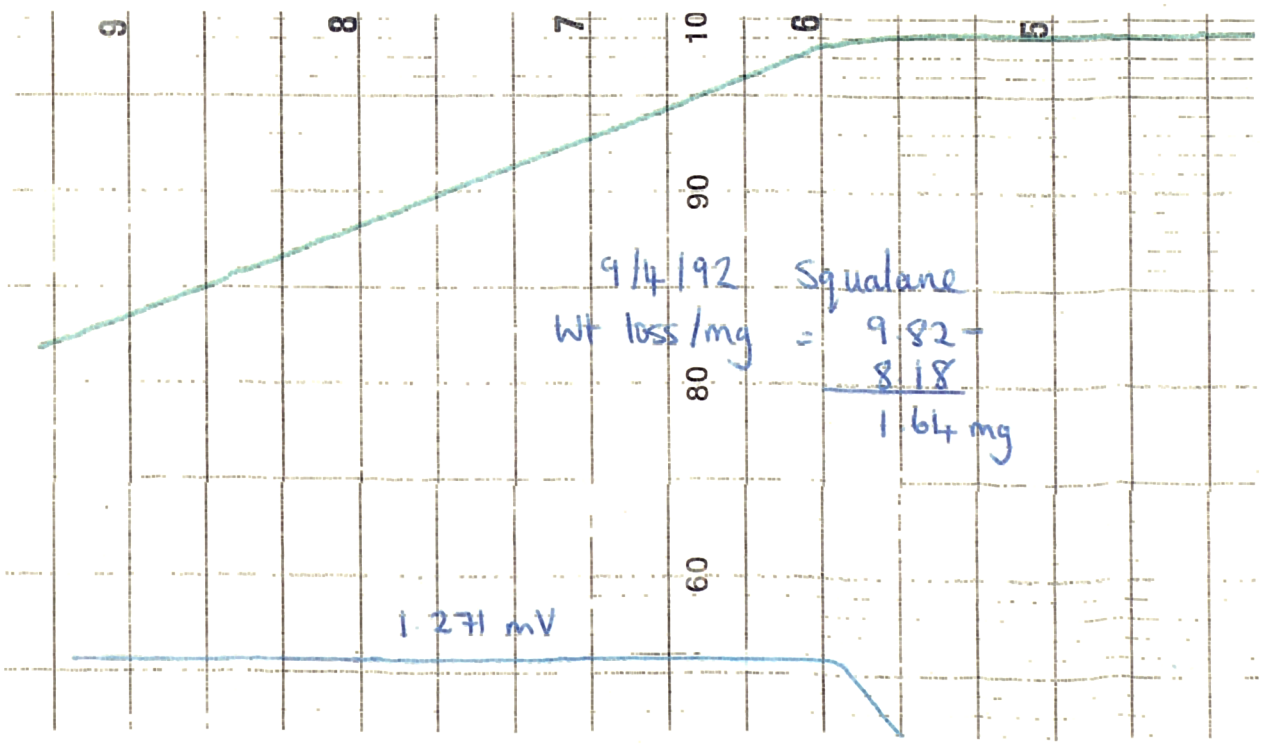


Figure 2.a

The isothermal temperature could not be determined as described earlier as the Stanton Redcroft TG-750 Thermal Analyser could not heat at 1°C/min. By heating squalane at 10°C/min to several isothermal temperatures and measuring the mass loss over a 30 minute period, the isothermal temperature was determined by the extrapolation of the mass loss versus the isothermal temperature graph, as shown in Figure 2.b.

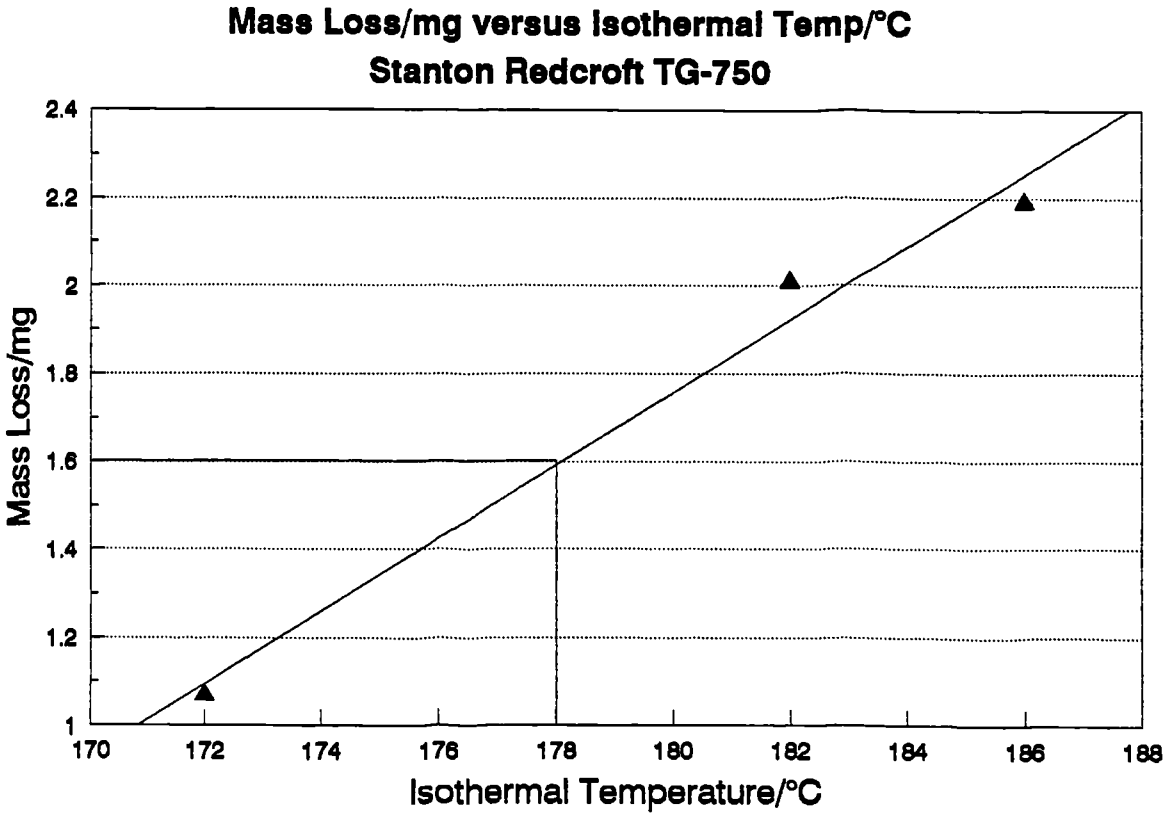


Figure 2.b

The isothermal temperature corresponding to a mass loss of 1.6mg was found to be 178°C. Squalane was then run repeatedly using the procedure described in 2.2.2. The results are given in Table 2.a.

Table 2.a

Run number	Mass Loss/mg
1	1.84
2	1.68
3	1.71
4	1.90
5	2.02
6	1.73
7	1.56
8	1.64
9	1.55
10	1.39
11	1.42
12	1.61

$$n=12 \quad \bar{x}=1.67 \quad \sigma_{n-1}=0.19 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=11.1 \ \%RSD$$

where n = *number experiments* $\bar{x}$ = *mean* σ_{n-1} = *standard deviation*

$$\textit{where} \quad \sigma_{n-1} = \sqrt{\sum_{n=i}^{n} \frac{(x_i-\bar{x})^2}{n-1}}$$

Assuming that the results have a normal distribution about the mean then the standard error is approximately twice the standard deviation. In the case above the standard error was therefore,

$$\textit{mass loss} = 1.67 \pm 0.4 \ \textit{mg}$$

The repeatability was not acceptable, the weight loss ranging from 1.39mg to 2.02mg for squalane. The main cause of error was concluded to be lack of temperature control, despite the efforts made to alleviate the problems.

A firm then agreed to loan their instrument to De Montfort University to complete the IP work. The instrument was easy to operate and could be programmed such that each experiment could be left to run by itself. The isothermal temperature was determined as described by the IP draft method and squalane was run repeatedly. A typical trace is shown in Figure 2.c.

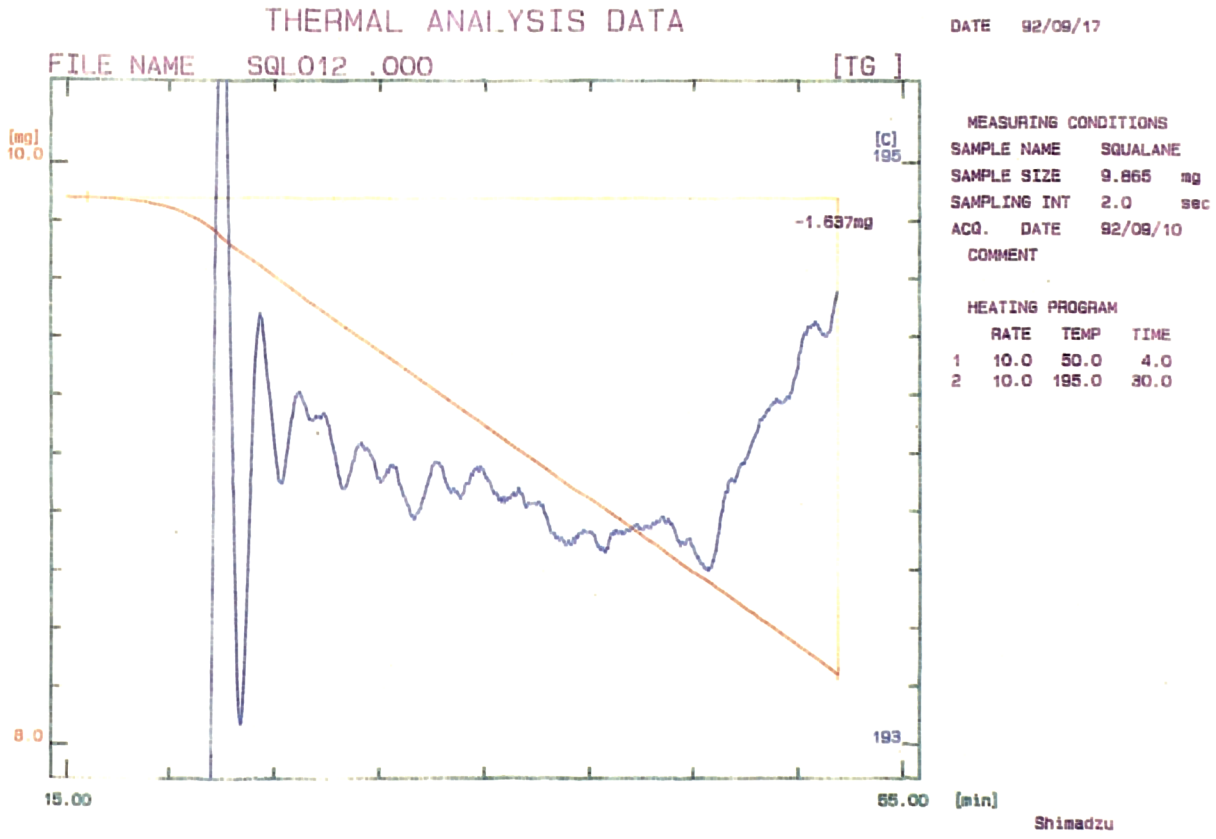


Figure 2.c

The results obtained from squalane are shown below.

Table 2.b

Run Number	Mass Loss/mg
1	1.63
2	1.72
3	1.71
4	1.61
5	1.54
6	1.64
7	1.64
8	1.80
9	1.66
10	1.42
11	1.43
12	1.46
13	1.49
14	1.71
15	1.52

where

$$n=15 \quad \bar{x}=1.60 \quad \sigma_{n-1}=0.12 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=7.3\ \%RSD$$

$$\therefore\ mass\ loss = 1.60 \pm 0.24\ mg$$

The mass loss for squalane ranged from 1.42mg to 1.80mg. Although significantly better than the Stanton Redcroft results the repeatability was not adequate. A closer examination of the TG traces showed that once the

isothermal temperature had been reached the temperature then drifted ± 0.2°C. Within five minutes from the end of the experiment the temperature increased by 0.8°C. The temperature controller was obviously inadequate for accurate isothermal methods. This was a fault of the instrument which is being examined by the manufacturers.

In December 1992 the University purchased a thermalanalyser from Marlin Scientific, Model TA 51. The isothermal temperature was determined, as described by the IP draft method, to be 191°C. The flat based cylindrical aluminium pans were used in the inverted position, as recommended by Marlin Scientific, to give a uniform surface area without side surface creep effects. A typical TG trace is shown below.

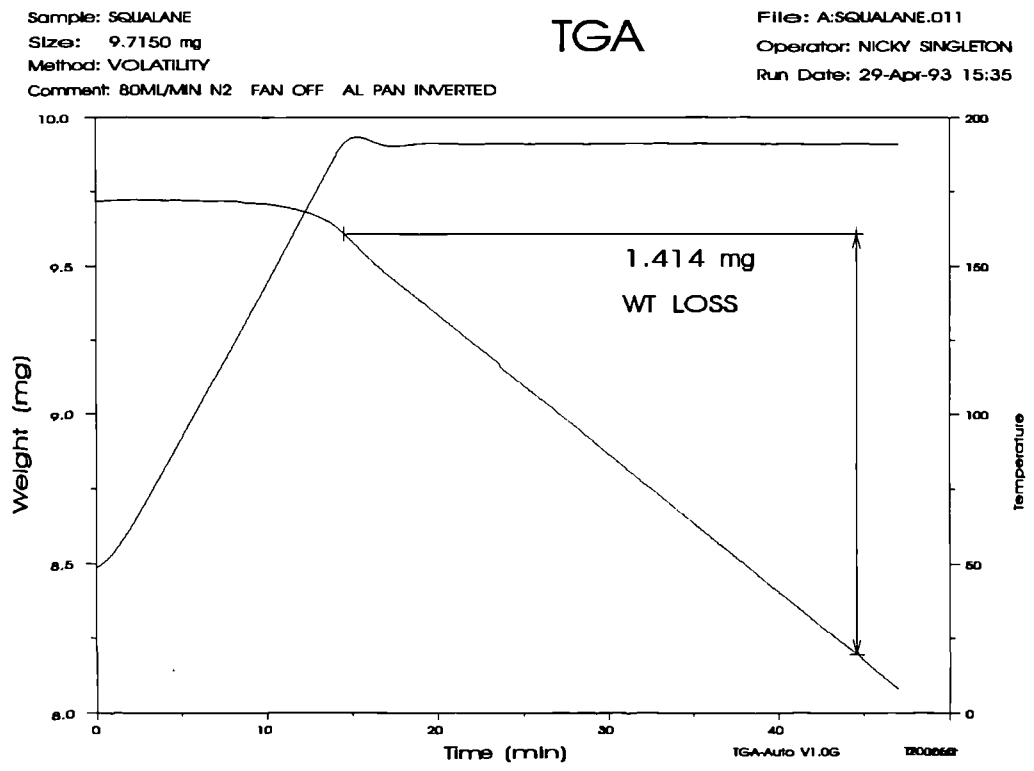


Figure 2.d

Results for repeat runs of squalane are given below

Table 2c

Run number	Mass Loss/mg
1	1.44
2	1.49
3	1.49
4	1.41
5	1.38
6	1.44
7	1.45
8	1.39
9	1.46
10	1.41

$$n=10 \quad \bar{x}=1.44 \quad \sigma_{n-1}=0.04 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=2.7\ \%RSD$$

$$\therefore\ mass\ loss = 1.44 \pm 0.08\ mg$$

The results ranged from 1.38mg to 1.49mg which was acceptable. Examination of the temperature profile showed that the isothermal temperature was maintained to within 0.04°C. This degree of accuracy in maintaining a fixed temperature is obviously required for the determination of oil volatility. The set of samples supplied for the round robin were then run in duplicates. The results are shown in Table 2.d.

Table 2.d

Filename	Mass Loss/mg	Relative Volatility	Date
STG9_54.001	2.19	1.52	20/1
STG9_54.002	2.19	1.52	20/1
STG9_78.001	0.90	0.63	21/1
STG9_78.002	0.87	0.60	21/1
STG9_79.001	1.56	1.08	21/1
STG9_79.002	1.52	1.06	21/1
STG9_80.001	3.01	2.09	21/1
STG9_80.002	2.92	2.03	21/1
STG9_81.001	2.95	2.05	22/1
STG9_81.002	2.80	1.94	22/1
STG9_81.003	2.95	2.05	30/4
STG9_81.004	3.1	2.15	30/4
STG9_83.001	1.01	0.70	25/1
STG9_83.002	1.03	0.72	25/1
STG9_84.001	1.35	0.94	25/1
STG9_84.002	1.30	0.90	25/1
STG9_85.001	2.96	2.06	26/1
STG9_85.002	2.88	2.00	26/1
STG9_86.001	2.13	1.48	26/1
STG9_86.002	2.10	1.46	26/1
STG9_87.001	0.80	0.56	26/1
STG9_87.002	0.81	0.56	26/1
STG9_90.001	2.16	1.50	27/1
STG9_90.002	2.15	1.49	27/1

These results have been reported to the IP Thermal Analysis Panel.

2.2.5 Discussion

The results obtained from the round robin experiments have been compared with those obtained by other laboratories. The results are shown below.

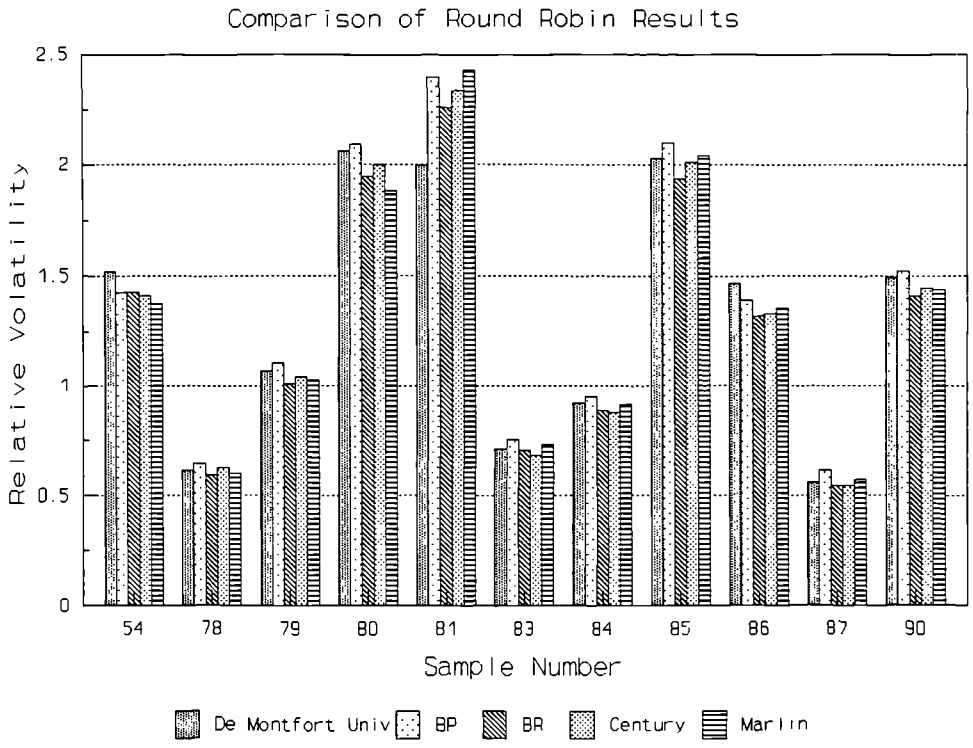


Figure 2.e

The results obtained by the IP panel looked promising. The result obtained by De Montfort University for sample 81 was low when compared with the results obtained from other laboratories. Repetition of this sample gave the same results as previously attained. The reason for this was thought to be due to the pan orientation. The other samples were analysed with the flat based pan in the inverted position, as recommended by Marlin Scientific. This was not possible with sample 81 as it flowed over the edge and therefore was analysed with the

pan in the normal upright position. The uncharacteristic results for sample 54 and 86 cannot be explained however. One possible source of error could be the temperature 'overshoot', the maximum temperature reached before a stable isothermal temperature was attained. Providing that the 'overshoot' was constant for each experiment would however eliminate this problem. Another source of error was static build-up, a recognised problem with sensitive balance mechanisms. To try and reduce this effect an earth wire was attached to the instrument at an appropriate position.

The relative volatility results obtained by BP and De Montfort University were slightly higher than the results obtained by the other laboratories. The mass loss for squalane was approximately 1.4mg, as determined by BP and De Montfort University, whereas the other laboratories obtained a mass loss nearer 1.6 mg. The mass loss of squalane therefore appears to influence the relative volatilities. Squalane is a pure hydrocarbon with a definite boiling point whereas mineral oils consist of many compounds of varying boiling points. The boiling range of a mineral oil can vary according to both its source and type of refining. When selecting a suitable isothermal temperature to give a specified mass loss for squalane, a relatively small change in temperature resulted in a relatively large change in mass loss. It was thought that this would not be the case with mineral oils. The reproducibility of the method could perhaps be improved by narrowing the allowed mass loss for squalane when determining the experimental conditions.

2.2.6 Conclusion

The round robin results obtained by several laboratories using the proposed thermogravimetric method were found to be promising.

2.3 Modified Methods

Two other methods were developed for the determination of oil volatility by thermogravimetry. The first (Method 1) was to allow for the use of Marlin Scientific "Solid Fat Index" (SFI) pans, and the second (Method 2) was developed to try and decrease the duration of the experiment.

2.3.1 Method 1

The draft IP method specifies that the sample size must be 10 mg ± 0.5 mg using a flat based cylindrical aluminium pan. The sample pans designed and supplied by Marlin Scientific for liquid samples are called SFI pans. They can hold approximately 4mg of oil sample. The difference between the two types can be seen in Figure 2.f, showing pans and sample position.

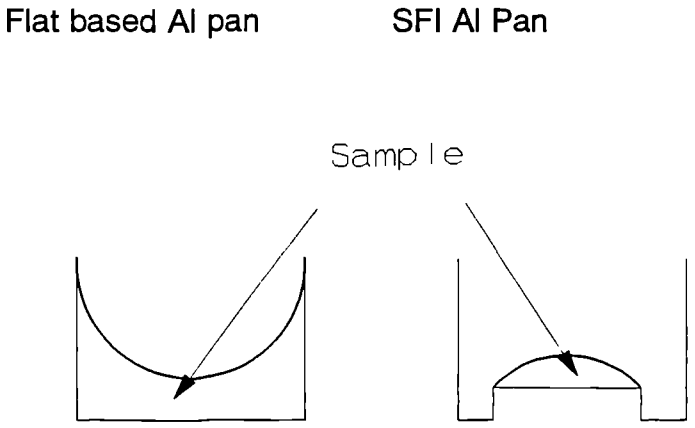


Figure 2.f

Unfortunately the SFI pans will not accommodate a 10mg sample without the sample overflowing into the 'moat'. This can be seen visually and is also confirmed with unusually high volatility results, due to the sudden increase in surface area. The maximum sample size when using the SFI pan was found to be 4mg. As the weight loss, as described by the IP draft method, was 1.4-1.8mg

for a 10.0mg sample (14-18%), a mass loss of 0.56-0.72mg for a 4 mg sample (14-18%) was expected, using the same isothermal temperature as before (191°C).

2.3.2 Results For Method 1

The results for squalane are given in Table 2.e.

Table 2.e

Run number	Mass Loss/mg
1	0.58
2	0.60
3	0.61
4	0.59
5	0.57
6	0.59
7	0.57
8	0.56
9	0.61
10	0.61

$$n=10 \quad \bar{x}=0.59 \quad \sigma_{n-1}=0.02 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=3.1 \ \%RSD$$

$$\therefore \ mass\ loss = 0.59 \pm 0.04\ mg$$

The results of the round robin samples are given in Table 2.f.

Table 2.f

Filename	Mass Loss/mg	Relative Volatility	Date
STG9_54.001	0.86	1.46	26/2/93
STG9_54.002	0.88	1.49	26/2/93
STG9_78.001	0.40	0.68	26/2/93
STG9_78.002	0.39	0.66	26/2/93
STG9_79.001	0.70	1.19	2/3/93
STG9_79.002	0.70	1.19	2/3/93
STG9_80.001	1.23	2.08	17/3/93
STG9_80.002	1.16	1.97	19/3/93
STG9_81.001	1.38	2.34	23/3/93
STG9_81.002	1.37	2.32	23/3/93
STG9_81.003	1.37	2.32	16/4/93
STG9_81.004	1.40	2.37	19/4/93
STG9_83.001	0.46	0.78	25/3/93
STG9_83.002	0.43	0.73	25/3/93
STG9_84.001	0.59	1.00	30/3/93
STG9_84.002	0.56	0.95	30/3/93
STG9_85.001	1.29	2.19	31/3/93
STG9_85.001	1.24	2.10	31/3/93
STG9_86.001	0.89	1.51	1/4/93
STG9_86.002	0.94	1.59	1/4/93
STG9_87.001	0.36	0.61	1/4/93
STG9_87.002	0.35	0.59	1/4/93
STG9_87.003	0.37	0.63	2/4/93
STG9_90.001	0.93	1.58	2/4/93
STG9_90.002	0.96	1.63	2/4/93

2.3.3 Method 2

The analysis time, using the IP draft method, for each sample was approximately 50 minutes, excluding cooling time in between each run. Running duplicates restricted the number of different samples to 3 or 4 a day. Examination of a typical TG trace showed that no mass loss occurred until 130°C. Once the isothermal temperature had stabilised the rate of mass loss was uniform. Based on these facts a significantly quicker method was developed. The heating program was as follows

1) Equilibrate at 100°C
2) Heat at 10°C/min to isothermal temperature
3) Hold at isothermal temperature for 15 minutes

The advantages of this method are

i) Decrease in cooling time in between runs
ii) Decrease in overall analysis time, approx 30 minutes

The isothermal temperature was determined as the temperature at which a 14-18% mass loss occurred over a 15 minute period for a 4mg sample.

2.3.4 Results For Method 2

The isothermal temperature was found to be 205°C. The results for squalane are given in Table 2.g.

Table 2.g

Run number	Mass Loss/mg
1	0.60
2	0.63
3	0.62
4	0.60
5	0.63
6	0.62
7	0.62
8	0.62
9	0.63
10	0.65

$$n=10 \quad \bar{x}=0.62 \quad \sigma_{n-1}=0.01 \quad \frac{\sigma_{n-1}}{\bar{x}} \times 100 = 2.4\ \%RSD$$

$$\therefore\ weight\ loss/\ mg\ =\ 0.62\ \pm\ 0.02$$

The IP round robin samples were run using Method 2, the results given in Table 2.h.

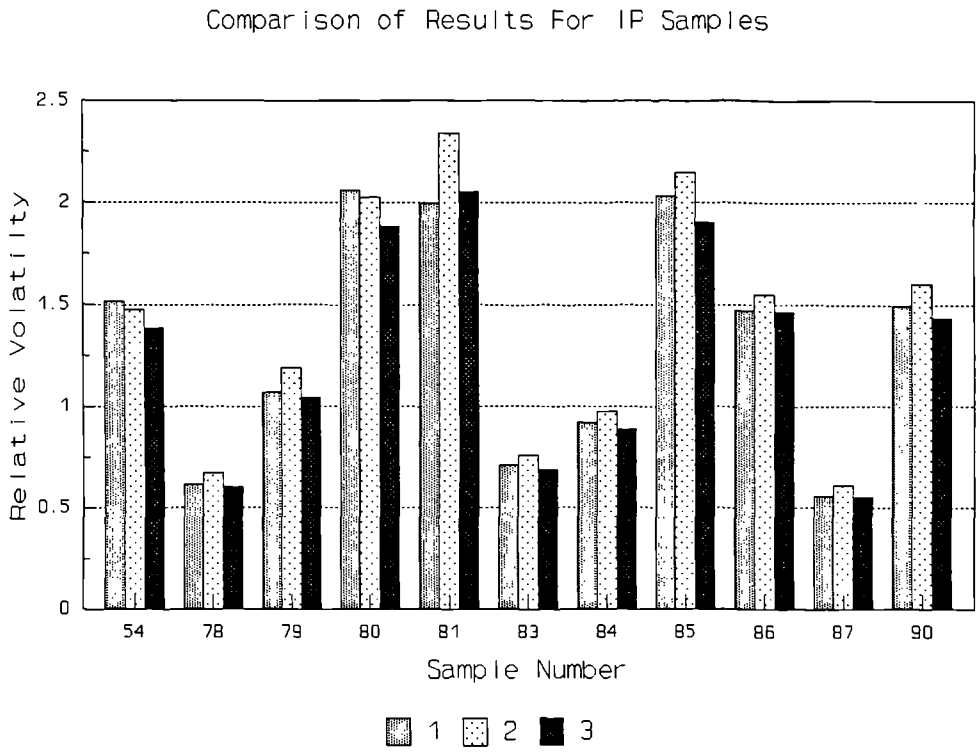
Table 2.h

Filename	Mass loss/mg	Rel. Vol.	Date
STG9_54.001	0.85	1.37	18/2/93
STG9_54.002	0.87	1.40	18/2/93
STG9_78.001	0.37	0.60	19/2/93
STG9_78.002	0.38	0.61	19/2/93
STG9_79.001	0.66	1.06	19/2/93
STG9_79.002	0.64	1.03	19/2/93
STG9_80.001	1.20	1.94	19/2/93
STG9_80.002	1.14	1.84	19/2/93
STG9_80.003	1.17	1.89	19/2/93
STG9_80.004	1.16	1.87	23/2/93
STG9_80.005	1.16	1.87	23/2/93
STG9_81.001	1.24	2.00	19/2/93
STG9_81.002	1.29	2.08	19/2/93
STG9_81.003	1.28	2.06	23/2/93
STG9_81.004	1.31	2.11	23/2/93
STG9_81.005	1.29	2.08	16/4/93
STG9_81.006	1.24	2.00	16/4/93
STG9_83.001	0.43	0.69	22/2/93
STG9_83.002	0.47	0.76	22/2/93
STG9_83.003	0.43	0.69	24/2/93
STG9_83.004	0.42	0.68	24/2/93
STG9_84.001	0.56	0.90	22/2/93
STG9_84.002	0.54	0.87	22/2/93
STG9_85.001	1.18	1.90	22/2/93
STG9_85.002	1.18	1.90	22/2/93
STG9_86.001	0.92	1.48	22/2/93
STG9_86.003	0.90	1.45	23/2/93
STG9_87.001	0.34	0.55	23/2/93
STG9_87.002	0.35	0.56	23/2/93
STG9_90.001	0.88	1.42	23/2/93
STG9_90.002	0.90	1.45	23/2/93

2.3.5 Discussion

The bar chart below compares the results obtained for the IP samples using the three methods described earlier, ie.

1) IP draft method 10mg samples, flat based pan
2) Method 1 4mg samples, SFI pan
3) Method 2 Quick, 4mg samples, SFI pan



The results show that in general the relative volatilities follow a trend:

Method 1 > IP Draft Method > Method 2

Although squalane is used as a standard to determine relative volatilities the results between methods can still differ. The repeatability however was good for

each method. As Method 2 was considerably quicker this method was preferred to analyse the used oils described later.

As discussed previously the IP round robin results indicated that the mass loss for squalane influenced the relative volatility results. This was investigated further using Method 2 where the mass loss for squalane and sample STG9/85 were determined at an isothermal temperature of 201°C, 203°C and 207°C. The relative volatilities of STG9/85 were then calculated at each different temperature, Table 2.i.

Table 2i

Temp/°C	Mass Loss/mg Squalane	Mass Loss/mg STG9/85	Relative Volatility STG9/85
201	0.47	1.03	2.191
203	0.57	1.13	1.982
205	0.62	1.18	1.903
207	0.68	1.26	1.853

Figure 2.h shows that the relative volatility decreases as the isothermal temperature increases. The standard error associated with each mass loss was ± 0.02mg which results in an error of ±0.04 for each relative volatility value. The relative volatility for sample 85 decreased from 2.191 to 1.982, a difference of 0.24, as the isothermal temperature was increased from 201°C to 203°C. As the isothermal temperature was further increased the change in relative volatility became less significant. Further experiments using a range of samples would be of interest, to further clarify this observation.

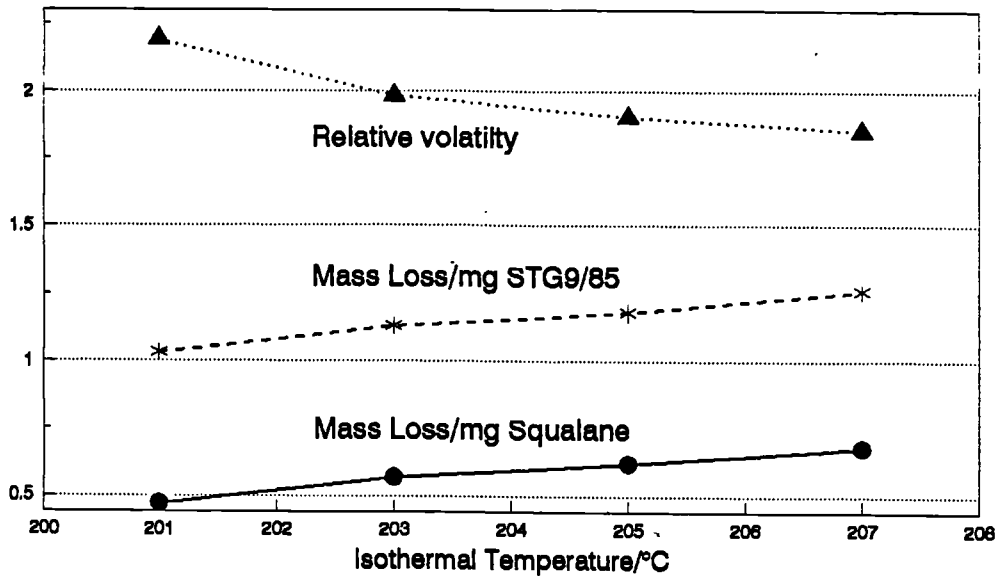


Figure 2.h

The Noack values for the round robin samples were distributed to the IP panel members and used to determine the correlation, if any, with the TG results. A plot of Noack value versus relative volatility as measured by Method 2 is shown below.

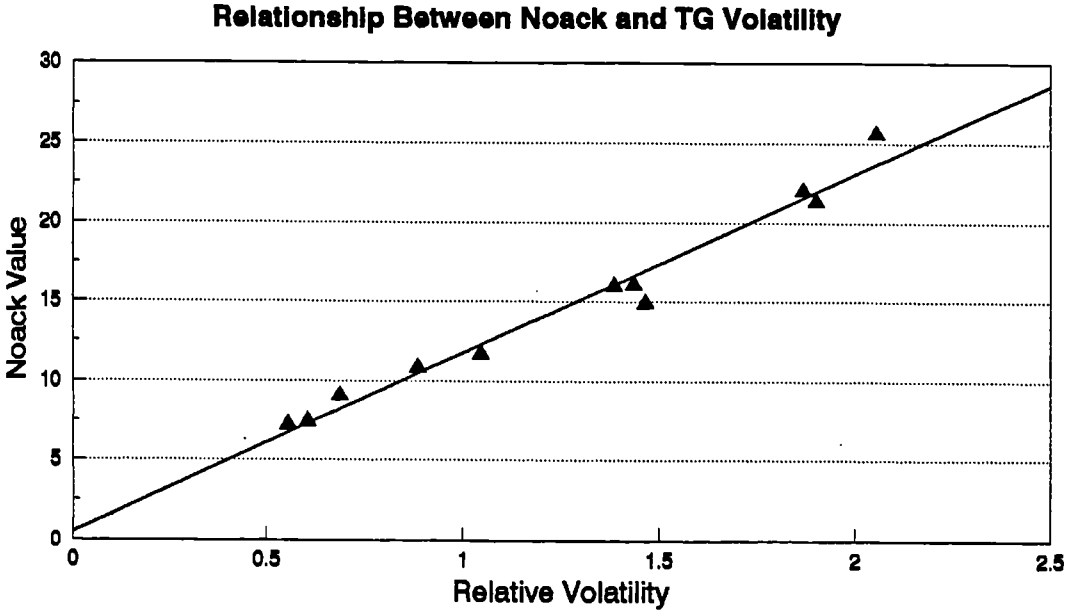


Figure 2.i

From the graph it can be seen that there is a linear relationship between the TG relative volatility and Noack results, although the graph does not quite pass through the origin. The best line fit was then calculated using a statistical package such that the graph passed through the origin, as would be expected. The relationship between Noack and relative volatility was found to be;

$$\textit{Noack} = \textit{Relative Volatility} \times 11.62$$

A plot of observed Noack versus predicted Noack is shown below;

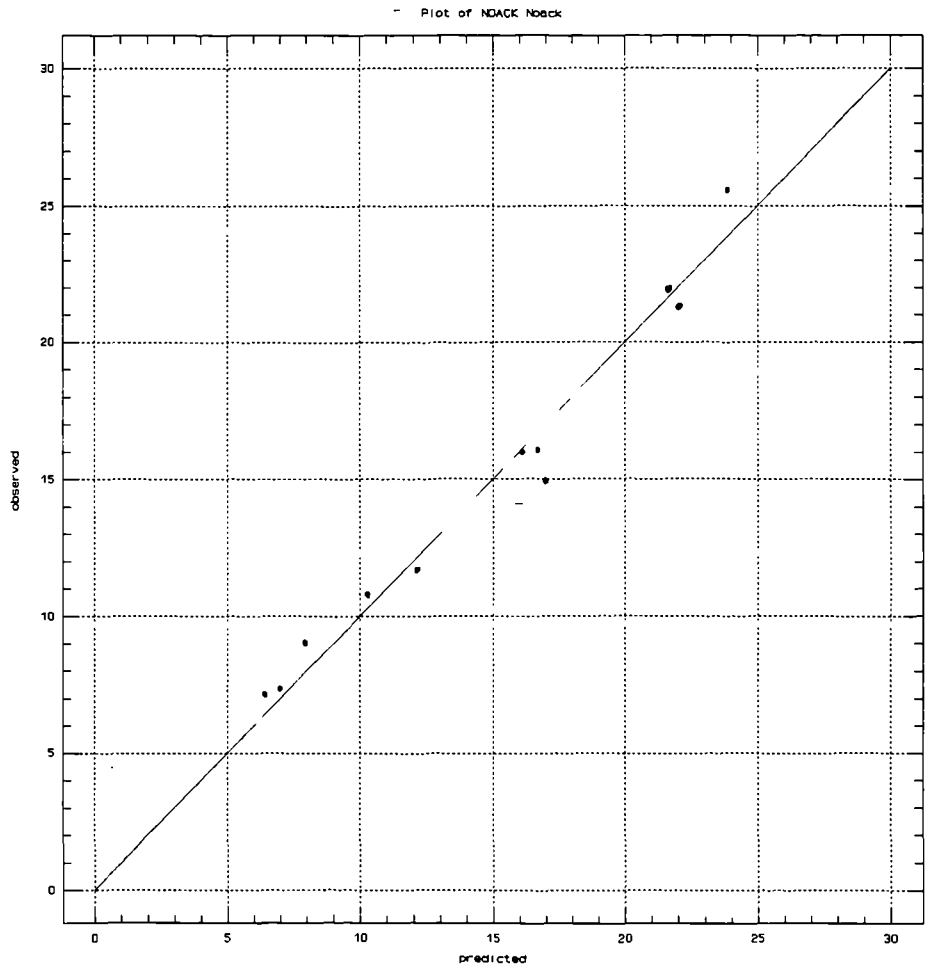


Figure 2.j

2.3.6 Conclusion

Repeatable results can be obtained with a sample size of 4mg using SFI pans, following the proposed IP method described in 2.2. A quicker thermogravimetric method has also been developed which reduces the analysis time from approximately 50 minutes to 30 minutes. The relative volatility results obtained from the round robin samples, using the quick TG method, were found to correlate well with their Noack results.

2.4 Used Oil Volatility

The used oils were analysed using the quick Method 2, described in **2.3.3.**

2.4.1 Description of Used Oils

Both gasoline and diesel oils were examined, as described below.

Diesel Oils

A Kuwait Petroleum low sulphur reference oil was run in a Petter AA1 at De Montfort University for 33 HRS. Top ring zone samples were collected every hour and then combined to give a large enough sample for several different analyses. Similarly the sump samples collected every hour were combined. The fresh, top ring zone and sump samples were named **Q8LSREF**, **Q8TRZ** and **Q8SUMP** respectively.

An Ethyl Petroleum mineral based multigrade oil was also run in the Petter AA1, only for 6 hrs. Top ring zone samples were collected every hour and a final sump sample was taken at the end of the run. As above the top ring zone samples were combined. The fresh, top ring zone and sump samples were named **ETHFSH**, **ETHTRZ** and **ETHSUMP** respectively.

The oil drained from a domestic diesel Peugeot 405 vehicle was collected and compared with the original fresh oil. The car had travelled approximately 10 000 miles before drainage, the bulk of which consisted of long distance journeys. The fresh and used oil samples were named **DAAFSH** and **DAASUMP** respectively.

Another oil supplied by Ethyl Petroleum was an end-of-engine-test oil, namely **ETH102E**. The corresponding fresh oil was not obtained, despite efforts to do so.

Gasoline Oils

A mineral based multigrade oil supplied by Castrol was tested in a Petter W1 at Castrol Research Centre for a duration of 108 hrs, samples collected every 36 hrs. The fresh oil and used oils were named **C370FSH**, **C37036**, **C37072** and **C370108**. The same fresh oil (**C370FSH**) was also run in a SAAB engine test, the end of test oil was named **SAABEOT**.

The oil drained from a Ford Escort after 6 000 miles was collected. The mileage consisted mainly of short journeys. The original oil was Shell Super, as bought from a garage. The fresh and drained oil were named **SHELLFSH** and **SHELLSUMP** respectively.

An end-of-engine-test oil was obtained from Ethyl Petroleum named **ETHNO6**. The fresh oil was not available.

2.4.2 Results

The average relative volatilities and predicted Noack values for the used oils are given in Table 2.j. The Noack values were calculated using the relationship given in **2.3.5**.

Table 2.j

Filename	Relative Volatility	Predicted Noack Values
Q8LSREF	1.435	16.7
Q8TRZ	0.992	11.5
Q8SUMP	1.363	15.8
ETHFSH	1.057	12.3
ETHTRZ	0.798	9.3
ETHSUMP	1.065	12.4
DAAFSH	1.210	14.1
DAASUMP	1.008	11.7
ETH102E	0.839	9.7
C370FSH	1.049	12.2
C37036	0.831	9.7
C37072	0.710	8.3
C370108	0.613	7.1
SAABEOT	1.000	11.6
SHELLFSH	1.073	12.5
SHELLSUMP	1.008	11.7
ETHNO6	1.476	17.2

2.4.3 Discussion of Results

The bar charts given in Figures 2.k and 2.l compare the results of the diesel and gasoline oil samples respectively.

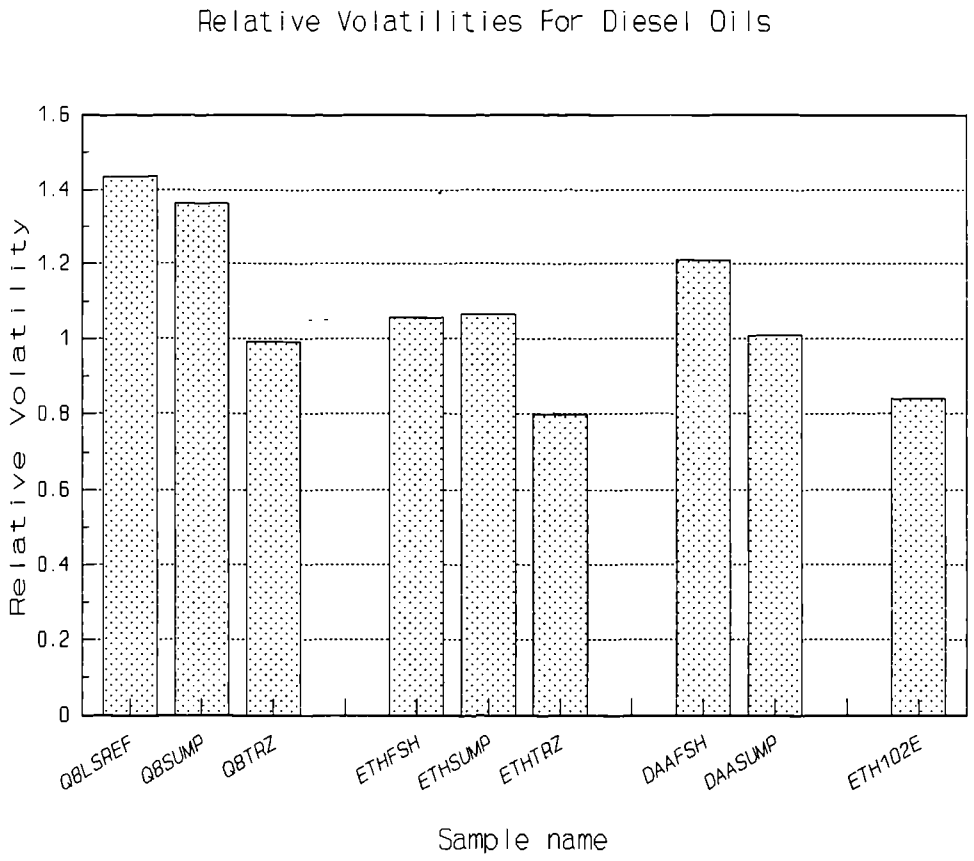


Figure 2.k

The diesel top ring zone samples have significantly lower relative volatilities than their corresponding fresh or sump samples. For example the relative volatilities of Q8TRZ (top ring zone)and Q8LSREF (fresh) were 0.992 and 1.435 respectively. The relative volatility of the top ring zone sample had decreased by 30%. The drop in relative volatility between the top ring zone samples and corresponding fresh samples were similar to the relative volatility drop between the fresh and Peugeot sump drain oil. Therefore samples taken from the top ring zone are comparable to the those obtained after 10,000 miles in a vehicle, in terms of relative volatility. The relative volatilities of top ring zone and ETH102E, the end of test oil, were also similar.

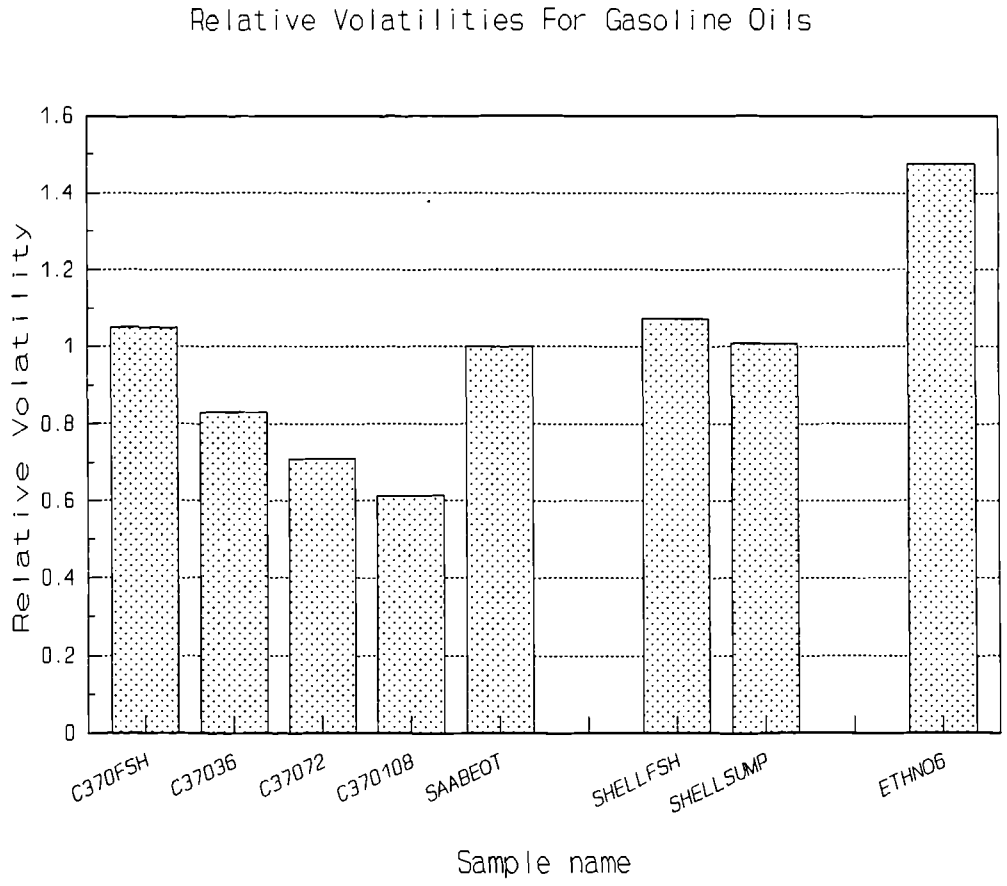


Figure 2.l

When comparing the Petter W1 samples collected at 36 hour intervals with the fresh oil (C370FSH) a distinct decrease in relative volatility is observed with increase in sampling time. The results obtained for the SAAB end of test oil, the Shell sump and Ethyl end of test oils therefore had significantly higher relative volatility results than expected. The TG traces for these oils were in fact different to those obtained previously. There was a significant mass loss prior to the temperature reaching the isothermal temperature (205°C). The TG traces obtained for C370FSH (typical oil) and SAABEOT are shown in Figures 2.m and 2.n respectively.

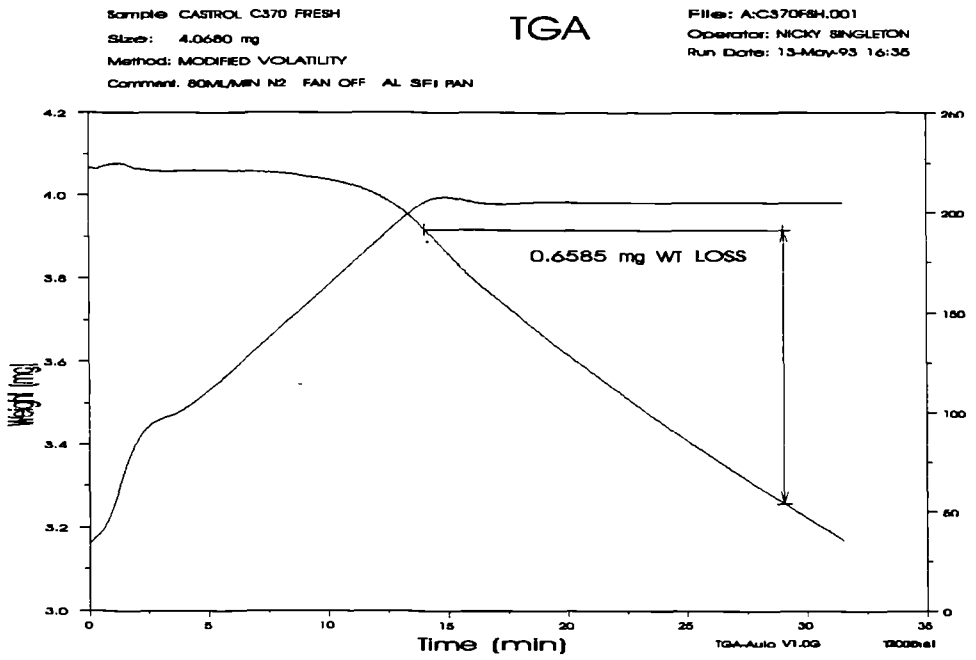


Figure 2.m TG Trace Sample C370FSH

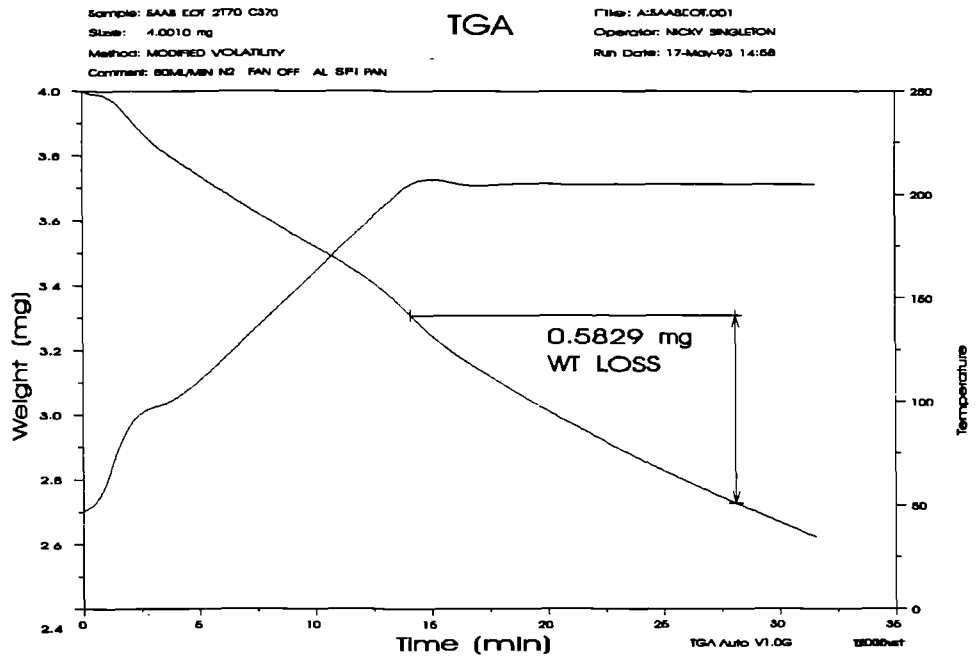


Figure 2.n TG Trace Sample SAABEOT

From the TG traces it is impossible to determine the nature of the more volatile components, which volatilise before the isothermal temperature is reached. The

weight loss could be due to fuel present in the oil or degradation products. The method was therefore not suitable for oil samples containing very volatile components such as fuel. A different temperature programmed method could perhaps be developed which could determine both fuel dilution and oil volatility.

It can be seen that the volatility of oils can decrease significantly during service. The samples taken from the top ring zone were found to have very low volatilities, resulting mainly from the loss of base oil. Loss of base oil alone would result in the concentration of the heavier fractions, including certain additives. It therefore becomes difficult to compare the used oils with their corresponding fresh oils, unless the evaporative losses are taken into consideration.

2.4.4 Conclusion

The diesel top ring zone samples were significantly less volatile than the corresponding sump and fresh oils. A decrease in volatility due to base oil loss would concentrate the less volatile components, such as the high molecular weight additives. It is therefore very important to take volatile losses into consideration when comparing fresh and degraded oils using other techniques, for example infrared analysis.

The TG method was not suitable for used oils containing very high volatile components, such as fuel.

CHAPTER 3 Conductimetric Non-Aqueous Titrations

3.1 Base Number Determination

3.1.1 Introduction

Lubricating oils can be contaminated with acidic compounds resulting from the combustion of fuel, particularly high sulphur diesel. If these compounds are allowed to accumulate they attack the internal surfaces and cause rapid corrosive wear. Alkaline (basic) substances are therefore added to neutralise the acids and minimize this type of wear. An oil's Base Number is a measure of the alkalinity present and gives an indication of the ability to counteract acidic contaminants. Base Number is expressed in terms of mg KOH/g oil, the equivalent weight, in milligrams of potassium hydroxide per gram of oil.

Methods for the determination of Base Number can be found in the Institute of Petroleum "Standard Methods For Analysis And Testing Of Petroleum And Related Products", IP 177 and IP 276. Both methods describe non-aqueous potentiometric procedures for the determination of Base Number. In the IP 177 method 0.1 mol dm^{-3} HCl (hydrochloric acid) in propan-2-ol (HCl_{alc}), is titrated against a sample of oil dissolved in a toluene/propan-2-ol/water (100:99:1) solvent mixture. In the IP 276 method 0.1 mol dm^{-3} $HClO_4$ (perchloric acid) in glacial acetic acid is titrated against a sample of oil dissolved in a glacial acetic acid/chlorobenzene (1:2) solvent mixture. The disadvantages of these methods include

1) Results vary according to method employed
2) Electrodes are difficult to maintain
3) Determination of the end point for used oils is very difficult

A significant amount of work has been carried out at De Montfort University using an alternative method for the determination of Base Number.

3.1.2 Development of New Base Number Method

The two methods described above were found to be inadequate for the analysis of the highly degraded oils obtained from the top ring zone of an engine. To improve end point determinations conductimetric titration experiments were carried out using the same solvent systems as those used in the IP methods. Initial results were very promising.

British Rail were, at that time, looking for a repeatable, reliable method for Base Number determination for inclusion in their oil condition monitoring program. This program monitored the degradation of oils over their service life. Collaborative work was carried out between De Montfort University and British Rail to compare the potentiometric and conductimetric analysis of oil samples using IP 276 solvent system. A range of fresh and used oils were analysed, with Base Numbers ranging from 5-40 mg KOH/g oil. For simplicity these oils will be referred to as SET-1. The oils were analysed by both potentiometric and conductimetric methods at the BR Research Centre, and by the conductimetric method at De Montfort University. The results from this study were discussed by Fakir [14]. The results showed excellent agreement between the two methods and between the two laboratories. The limited number of determinations using IP 177 solvent system showed good repeatability. A reproducibility study using SET-1 oils was then organised including government, academic, industrial and railway establishments. The results showed excellent agreement between laboratories.

Due to the successful results obtained using the manual conductimetric method, a prototype automated Base Number (BN) apparatus was built by De Montfort University. The details of the prototype and studies made were discussed by

Pickering [15], summarised below.

Repeatability and reproducibility studies for the automated apparatus were carried out using the oil samples previously mentioned, SET-1, plus an additional quality control fresh oil sample. The IP 276 solvent system was used for the majority of Base Number determinations. A limited number of determinations were made using the IP 177 solvent and a new IP proposed solvent called the "Trisolvent". Results obtained using the automated apparatus were compared with those obtained in the earlier studies made on the SET-1 oil samples. The agreement between results obtained for the same sample using the automatic conductimetric method using all solvents was excellent. When comparing the manual and automatic conductimetric methods, agreement between Base Number values obtained for the same samples was again excellent. Comparison of BN results determined by the conductimetric and potentiometric methods showed that for the IP 276 solvent system excellent agreement was observed, for IP 177 solvent system excellent agreement was observed for fresh oils but not used oils, and for the "Trisolvent" the conductimetric results were higher than those obtained from the potentiometric method.

A program of work based on the analyses of a large number of samples (over 200) was undertaken. The samples were from a number of industrial establishments (British rail, Burmah Castrol, Century Oil and Lubrizol), the Base Numbers of which had already been determined using potentiometric methods in their own laboratories. Three of the four laboratories used IP 276 solvent, the fourth using IP 177 solvent. These samples were analysed using the automated prototype, with the appropriate solvent. The results of the study showed that the conductimetric method gave BN values which compared favourably with those obtained commercially using standard IP methods. The results obtained by De Montfort University using IP 276 were slightly higher than those determined industrially. The agreement between results obtained using IP 177 solvent were surprisingly poor. Further investigation showed that the end-point interpretation

using the potentiometric method seemed to be inconsistent and did not correspond to the same end-point using the conductimetric method. This was considered to be a problem for the laboratory concerned.

At this point the Base Number instrument was ready for commercial production.

3.2 Acid Number Determination

3.2.1 Introduction

As mentioned earlier lubricating oils can become contaminated with acidic compounds which are detrimental to the condition of the engine. These constituents are characterised by the Acid Number. As an oil degrades the Acid Number increases, whereas the Base Number decreases. The Acid Number is expressed as mg KOH/g oil, the equivalent mass of potassium hydroxide in milligrams required to neutralise the acidic constituents per gram of oil.

Methods for the determination of Acid Number can be found in the IP "Standard Methods For Analysis And Testing Of Petroleum And Related Products", IP 139 and IP 177. The IP 139 method is a colorimetric method which uses p-naphtholbenzein as the indicator. This method is not suitable for heavily discoloured oils. The IP 177 method describes a potentiometric titration, where 0.1mol dm^{-3} KOH (potassium hydroxide) in propan-2-ol (KOH_{alc}) is titrated against a sample dissolved in the IP 177 solvent system. The disadvantages of this method are the same as those experienced for the Base Number determination described earlier. In many cases the end-point is even more difficult to determine for this method than for the Base Number method.

Following the success of the conductimetric method developed at De Montfort University work was carried out to devise a more reliable method for Acid Number determination.

3.2.2 Development of New Acid Number

A method based on thermal analysis was considered by Fakir [14] which followed a reaction by recording its temperature. The reaction studied was the base catalysed polymerisation of acrylonitrile. The temperature of the solution remained constant until all the acidic component had reacted with the base added, at which point the temperature rose due to the initiation of the polymerisation reaction. Although very promising this method was not pursued as such a different method would almost definitely not gain industrial approval, based on previous experience.

As the IP 177 method also describes Acid Number determination by a potentiometric procedure, the determination by conductimetric end-point seemed an obvious alternative. A series of experiments were undertaken by Pickering [15] to develop a conductimetric Acid Number method. The titration of $KOH_{(alc)}$ against an oil sample in IP 177 solvent, using a conductimetric end point determination, was found to be totally unsatisfactory. This strange observation, when considering the success of the Base Number conductimetric method, was further investigated. The results are discussed by Pickering [15].

After considerable efforts a back titration method using IP 177 solvent system was found to be the most successful. A semi-automatic system capable of collecting and storing data and controlling the titrant additions was constructed for the purposes of these studies. The method, in summary, consisted of the titration of an oil sample dissolved in IP 177 solvent using 0.1 mol dm^{-3} $HCl_{(alc)}$ followed by a back-titration using 0.1 mol dm^{-3} $KOH_{(alc)}$. Although this method appears to be a viable alternative to the potentiometric Acid Number method a significant amount of work is required to prove the repeatability and reproducibility of the method. A range of samples of known Acid Number are required.

3.3 Recent Developments

Since the work of Pickering [15] the semi-automatic apparatus has been used for the determination of Base Numbers and speculative Acid Numbers of oil samples by both undergraduate and research students.

In the work described in this thesis a few studies were made initially in order to become familiar with the semi-automatic apparatus. Work was then carried out for the Institute of Petroleum (IP), where round robin samples were analysed using the Base Number method developed at De Montfort University, using both IP177 and IP 276 solvent systems. Used oils were then analysed to determine both their Base and Acid Numbers.

3.3.1 Effect of Solvent Volume

The amount of solvent used to dissolve the oil sample must be enough to cover the platinum plates of the electrode. The amount of solvent required to do this depends on the dimensions of the sample container. A few experiments were carried out where 0.1 mol dm^{-3} $HCl_{(alc)}$ was added to measured amounts of IP 177 solvent, with no oil sample, in 0.1 ml additions.

The results are given in Figure 3.a, where the conductance is plotted against volume of acid added for the different volumes of IP 177 solvent used. The volumes of solvent used were 18, 20, 25, 30, 40, 50 and 70 ml. The results show that the conductance rise is greatest for the smallest volume of IP 177 solvent used for the experiment. Larger volumes of solvent increase the dilution of the acid.

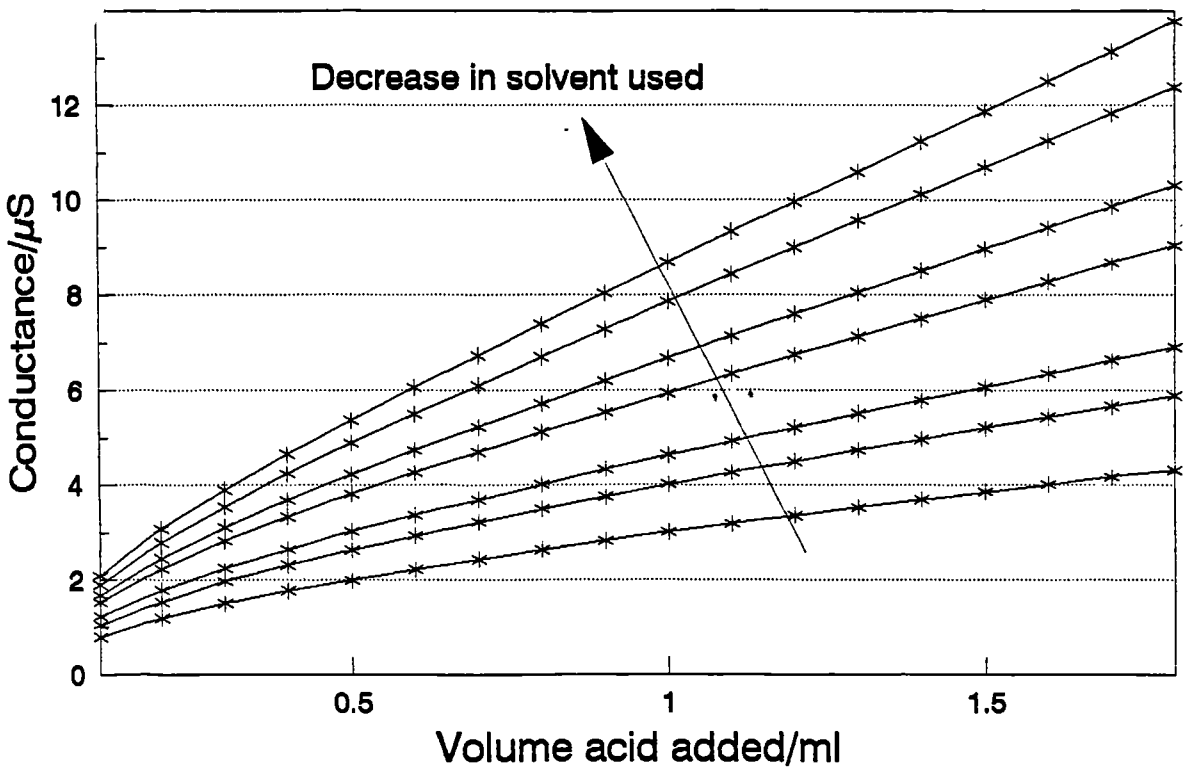


Figure 3.a

In order to obtain a sharp increase in conductance beyond the end-point of a titration the smallest amount of solvent must be used.

3.3.2 Rate of Stirring Effects

The rate of stirring is set by the user prior to titration. Experiments were carried out where the rate of stirring was different during each titration. By plotting the conductance versus the volume of acid added the difference between adequate (smooth curve) and inadequate (erratic curve) stirring can be seen. The results are given below in Figure 3.b.

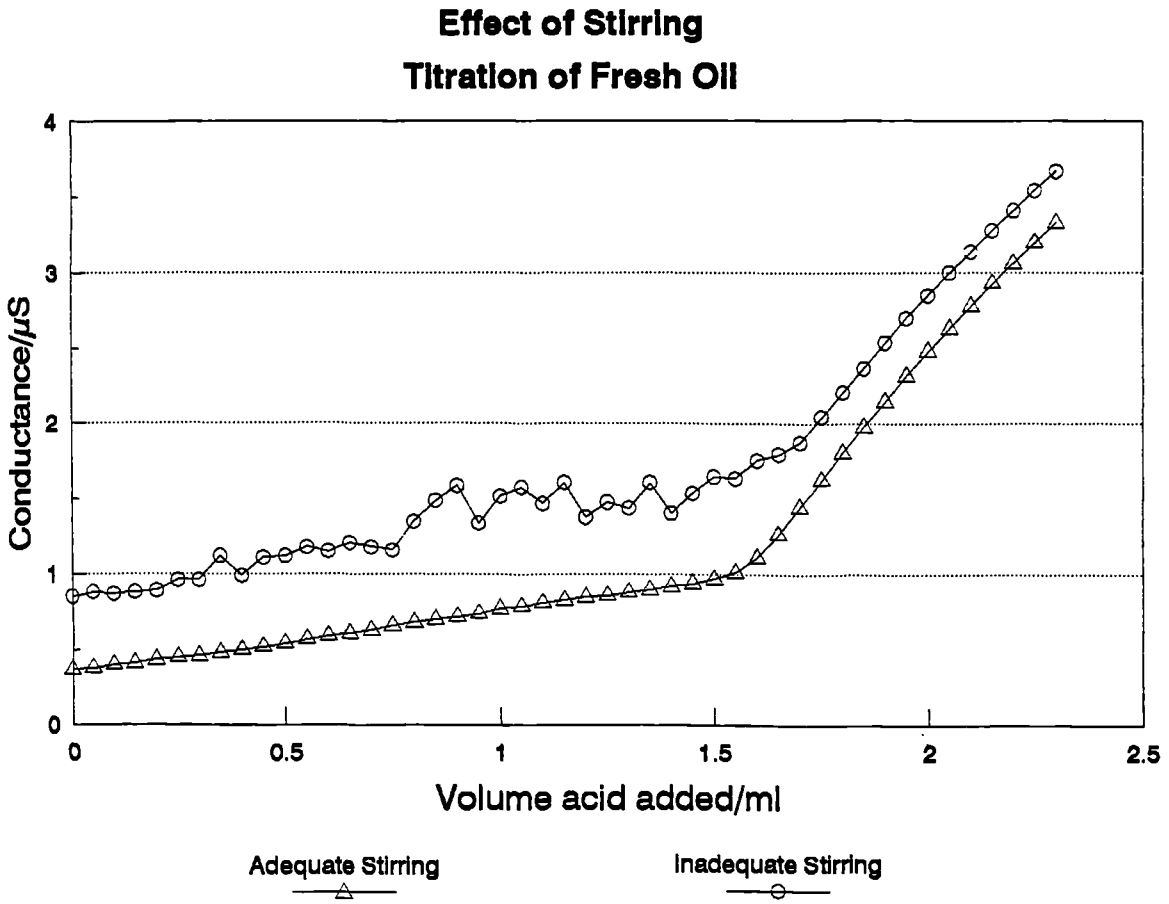


Figure 3.b

In order to obtain a smooth titration curve the sample must be sufficiently mixed throughout the experiment.

3.4 Work For The Institute of Petroleum

The Institute of Petroleum are currently developing a conductimetric method for the determination of Base Number. A set of oil samples labelled A-G were distributed to those laboratories, including De Montfort University, wishing to participate in a round robin. The work carried out is described below.

3.4.1 Method Using IP 177 Solvent

The acid $HCl_{(alc)}$ was first standardised using $KOH_{(alc)}$, which had previously been standardised using potassium hydrogen phthalate (KHP), $COOH(C_6H_4)COOK$ as follows. Approximately 0.1g of KHP was dissolved in distilled water, ensuring that the Pt plates of the electrode were totally immersed. 0.1 ml additions of $KOH_{(alc)}$ were made whilst continually stirring the mixture . After the completion of the titration the electrode and sample jar were rinsed in distilled water and IP 177 solvent until clean. The molarity of the $KOH_{(alc)}$ was calculated from the amount of base required to neutralise the KHP present. This was determined from the plot of conductance versus base added. Several experiments were carried out until concordant results were obtained. The $KOH_{(alc)}$ was then titrated against a known volume of $HCl_{(alc)}$ in IP 177 solvent. The molarity of the acid was then calculated from the amount of base required to neutralise the acid.

Each oil sample was dissolved in the minimum amount of IP 177 solvent in the sample container and placed onto the stirring plate. The electrode was gently lowered into the mixture such that the Pt plates were covered, whilst stirring continuously. The standardised acid was then added from the burette at 0.1 ml intervals until the conductance had risen well beyond the end-point. Inspection of the conductance versus acid volume plot enabled the Base Number to be calculated from the amount of acid required to reach the end-point of the titration. Each oil was run in duplicate.

3.4.2 Results

Standardisation of Base

$$moles\ KHP = \frac{mass_{KHP}}{204.22}$$

where $mass_{KHP}$ = mass potassium hydrogen phthalate/g

204.22 = relative molecular mass KHP

$$moles\ KOH = \frac{m_{KOH} \times v_{KOH}}{1000}$$

where m_{KOH} = molarity of $KOH_{(alc)}$ / mol dm^{-3}

v_{KOH} = volume $KOH_{(alc)}$ / ml at end-point

$$\therefore \quad m_{KOH} = \frac{mass_{KHP} \times 1000}{204.22 \times v_{KOH}}$$

Using the above calculation the following results were obtained

Molarity $KOH_{(alc)}$ = 0.082, 0.083, 0.082, 0.082 mol dm^{-3}

Average molarity $KOH_{(alc)}$ = 0.082 mol dm^{-3}

Acid Standardisation

$$moles\ HCl = \frac{m_{HCl} \times v_{HCl}}{1000}$$

where m_{HCl} = molarity $HCl_{(alc)}$ / mol dm^{-3}

v_{HCl} = volume $HCl_{(alc)}$ / ml to end-point

$$moles\ KOH = \frac{m_{KOH} \times v_{KOH}}{1000}$$

$$\therefore \quad m_{HCl} = \frac{m_{KOH} \times v_{KOH}}{v_{HCl}}$$

The molarity of $HCl_{(alc)}$ was found to be 0.102 mol dm^{-3}

Base Number

The Base Number was calculated as follows.

$$moles\ of\ HCl = \frac{m_{HCl} \times v_{HCl}}{1000}$$

where m_{HCl} = molarity of acid added/mol dm^{-3}

v_{HCl} = volume acid added/ml to end-point

$$moles\ KOH = \frac{mass_{KOH}}{56.1}$$

where $mass_{KOH}$ = mass of KOH/g

56.1= molecular mass KOH

$$\therefore \quad \frac{mass_{KOH}}{56.1} = \frac{m_{HCl} \times v_{HCl}}{1000}$$

$$\therefore \quad mass_{KOH} = \frac{m_{HCl} \times v_{HCl}}{1000} \times 56.1$$

$$\therefore \quad base\ number = \frac{m_{HCl} \times v_{HCl} \times 56.1}{mass_{oil}}$$

where Base Number = mg KOH/g oil, the equivalent mass in milligrams of KOH required to neutralise 1g of oil.

The Base Number results obtained at De Montfort University for the round robin samples are given in Table 3.a.

Table 3.a

	Base Number/ mg KOH/g oil	
	Result 1	Result 2
Sample E	16.0	16.0
Sample G	25.0	25.0
Sample F	40.8	41.2
Sample D	9.3	9.3
Sample H	17.6	17.7
Sample A	4.4	4.6
Sample C	29.8	29.7
Sample B	3.1	3.1

A typical graph of conductance versus acid added is shown in Figure 3.c.

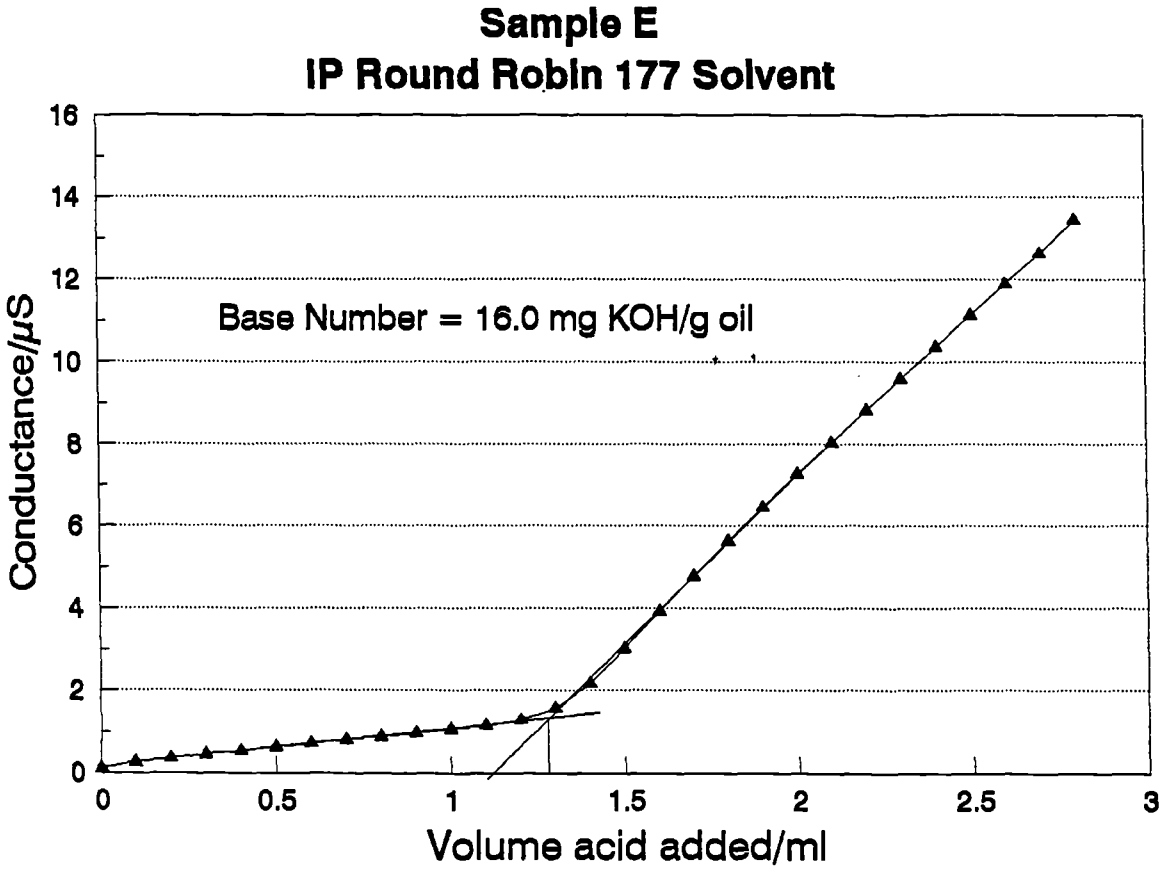


Figure 3.c

As the acid is added the conductance gradually increases until all the basic constituents have been titrated. The conductance then increases rapidly as excess acid is added to the solvent mixture.

3.4.3 Method Using IP 276 Solvent System

The $HClO_{4\ (ace)}$ was standardised directly with KHP. Approximately 0.1 g KHP was dissolved in the minimum amount of glacial acetic acid by gently warming on a hotplate. The IP 276 solvent was then added such that the Pt plates of the electrode would be covered. $HClO_{4\ (ace)}$ was added at 0.1 ml intervals with continual stirring. The molarity was calculated from the amount of acid required to neutralise the KHP. Samples A-H were then dissolved in the minimum amount of IP 276 solvent and titrated as above.

3.4.4 Results

Using a similar equation as previously described for the $HCl_{(alc)}$ standardisation the perchloric acid molarity was found to be 0.1008 and 0.1001 mol dm^{-3} respectively. The average molarity was 0.100 mol dm^{-3}.

The Base Numbers of the round robin samples are given in Table 3.b. Results were not obtained by other laboratories as the IP276 solvent system was not of interest to the IP.

Table 3.b

	Base Number/ mg KOH/g oil	
	Result 1	Result 2
Sample E	15.7	16.6
Sample G	24.9	25.4
Sample F	41.4	41.1
Sample D	11.0	11.4
Sample H	18.5	19.1
Sample A	7.7	7.6
Sample C	28	30.9
Sample B	3.3	2.8

A typical titration trace is shown below.

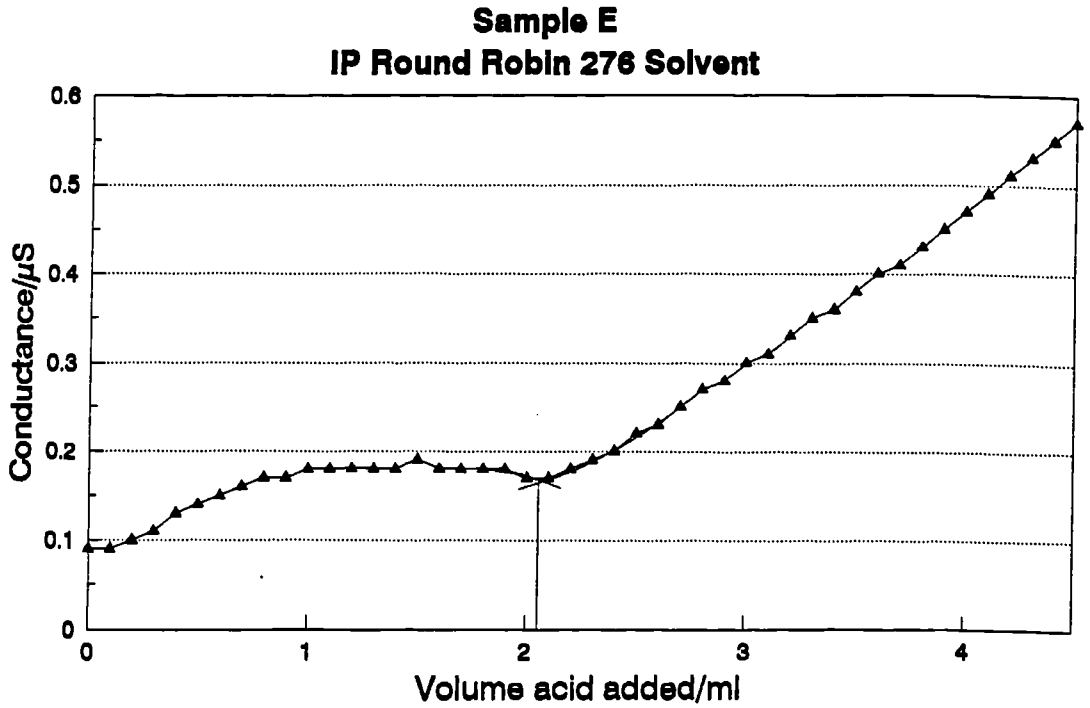


Figure 3.d

The conductance initially increases as the acid is added, then remains constant and then drops slightly before there is a rapid increase in conductance.

3.4.5 Discussion

A comparison of results obtained by the laboratories participating in the round robin is given in Figure 3.e, including the results from De Montfort University (lab 6). Each cluster represents the results obtained by all the participating laboratories for one oil sample.

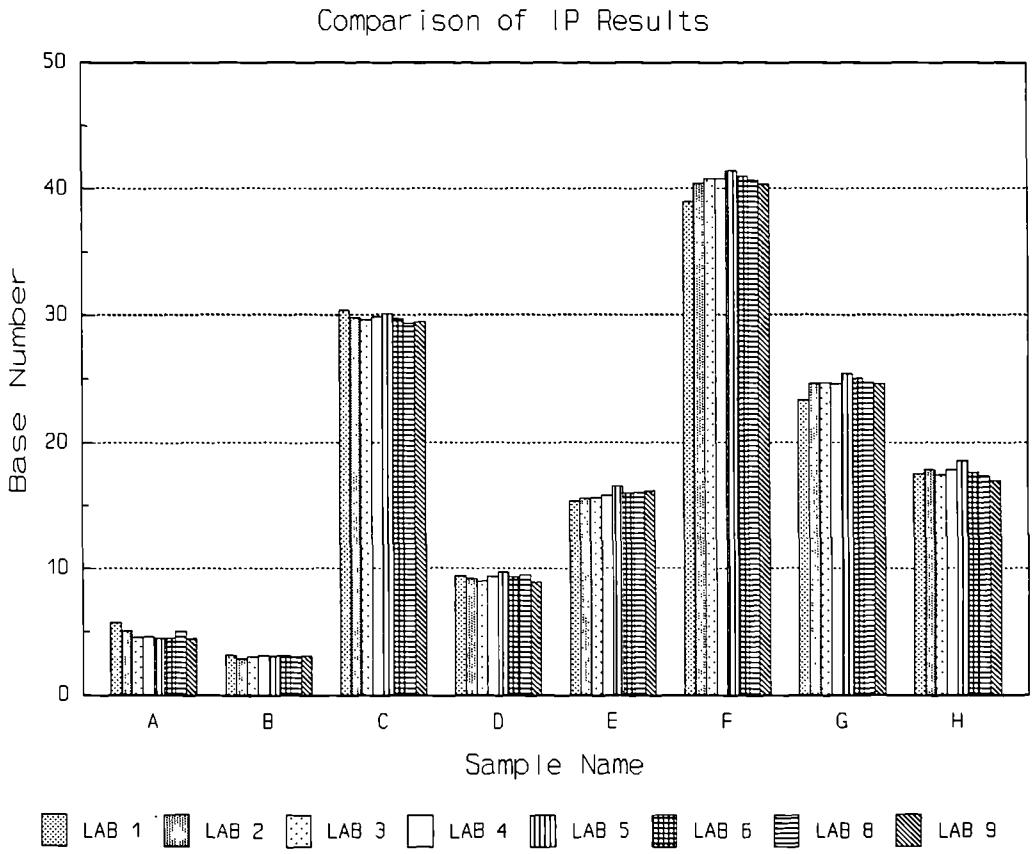


Figure 3.e

The results show that the conductimetric method, using IP 177 solvent, is both repeatable and reproducible, as shown by collaborative work between De Montfort University and British Rail a few years ago.

The results using IP 276 solvent were found to be less repeatable. This was primarily due to the poor resolution of the conductance meter. Using IP 177 the conductivity ranges from 0.01 - 20 μS during a typical titration whereas the conductivity ranges from 0.01 - 1 μS for a typical IP 276 titration. Increasing the sensitivity of the conductance meter seemed unnecessary for the few samples analysed above. Nevertheless the results were adequate to compare the results between IP 177 and IP 276 solvents. Taking the average values of the two results obtained using both methods a comparison has been made as shown in Figure 3.f.

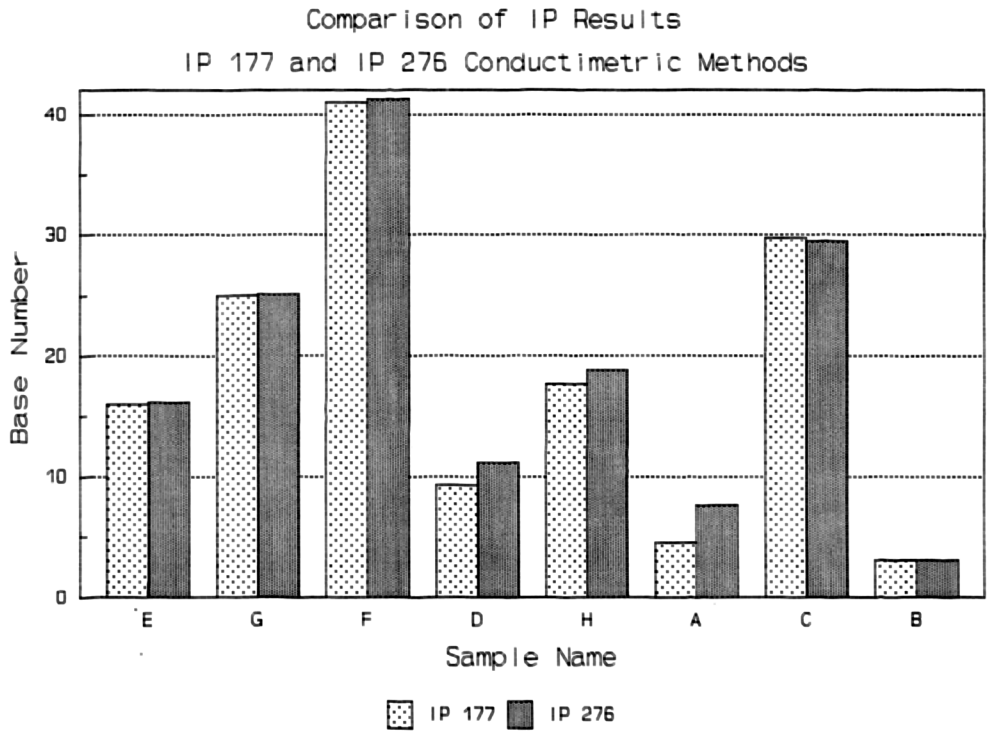


Figure 3.f

Samples D, H and A have a significantly higher Base Number using IP 276 as opposed to IP 177 solvent system. These samples are in fact the only used samples analysed. $HClO_{4(ace)}$ reacts with more constituents in the used oil samples than HCl_{alc}, $HClO_{4(ace)}$ being the stronger acid. Using IP 276 therefore gives an over estimate of the Base Number.

3.4.6 Conclusion

The Base Number determination method by conductimetric titration is both repeatable and reproducable, as demonstrated by the work carried out for the Institute of Petroleum. The IP 276 solvent system tends to record higher results for used oils than the IP 177 solvent system.

3.5 Analysis of Used Oil Samples

3.5.1 Introduction

The set of oils analysed using the semi-automatic titrator were those mentioned previously in Chapter 2, as given below.

Sample Name	Description
Q8LSREF	Fresh diesel multigrade oil supplied by Kuwait Pet.
Q8TRZ	Q8LSREF run in Petter AA1, top ring zone sample
Q8SUMP	Q8LSREF run in Petter AA1, sump sample
ETHFSH	Fresh diesel oil supplied by Ethyl Pet.
ETHTRZ	ETHTRZ run in Petter AA1, top ring zone sample
ETHSUMP	ETHTRZ run in Petter AA1, sump sample
DAAFSH	Fresh diesel oil
DAASUMP	Above oil taken from Peugeot 405 car after 10 000 miles
ETH102E	End of engine test diesel oil supplied by Ethyl Pet.

Sample Name	Description
C370FSH	Fresh gasoline multigrade oil supplied by Castrol
C37036	Sample taken from sump of Petter W1 engine test after 36 hrs, fresh oil C370FSH
C37072	Sample taken from sump of Petter W1 engine test after 72 hrs, fresh oil C370FSH
C370108	Sample taken from sump of Petter W1 engine test after 108 hrs, fresh oil C370FSH
SAABEOT	End of SAAB engine test, fresh oil C370FSH
SHELLFSH	Shell gasoline multigrade, as bought from shop
SHELLSUMP	Above oil taken from sump of Ford Escort after 6 000 miles
ETHNO6	End of engine test oil supplied by Ethyl

3.5.2 Method

Initially 0.1 mol dm^{-3} $HClO_{4(ace)}$ was titrated against each oil sample dissolved in IP 276 solvent. The $HClO_{4(ace)}$ had previously been standardised for the titration of the IP round robin samples. Fresh 0.1 mol dm^{-3} $KOH_{(alc)}$ and 0.1 mol dm^{-3} $HCl_{(alc)}$ were then made up as described in the IP 177 method and standardised. Approximately 0.1 KHP was used to standardise the $KOH_{(alc)}$, which was then titrated against a known volume of $HCl_{(alc)}$ as described in 3.4.1. The oil samples were then analysed using the back titration method mentioned in 3.2.2. The oil sample was dissolved in the minimum volume of IP 177 solvent with continual stirring. $HCl_{(alc)}$ was first added in approximately 0.1 ml additions until the conductivity had risen well beyond the Base Number end-point. $KOH_{(alc)}$ was then added in 0.1 ml additions until a steady increase in conductivity was observed. Between sample runs the apparatus was thoroughly cleaned.

3.5.3 Results

IP 276 conductimetric method

Table 3.c

	Base Number/ mg KOH/g oil	
Sample Name	Result 1	Result 2
Q8LSREF	11.6	11.7
Q8TRZ	15.4	15.2
Q8SUMP	11.6	11.6
ETHFSH	10.2	10.2
ETHTRZ	12.5	13.2
ETHSUMP	10.8	10.6
DAAFSH	10.0	9.9
DAASUMP	9.7	9.4
ETH102E	15.8	15.6
C370FSH	8.6	8.4
C37036	11.3	11.3
C37072	12.5	12.2
C370108	13.0	12.9
SAABEOT	5.0	4.7
SHELLFSH	7.4	7.2
SHELLSUMP	4.4	3.9
ETHNO6	4.0 / 3.3 / 4.5	3.9 / 4.7

IP 177 Conductimetric Back titration

Average molarity $KOH_{(alc)}$ = (0.096 + 0.096 + 0.096)/3 mol dm^{-3}

= 0.096 mol dm^{-3}

Average molarity $HCl_{(alc)}$ = (0.104 + 0.103 + 0.103 + 0.104 + 0.103)/5 mol dm^{-3}

= 0.103 mol dm^{-3}

A typical result using the back titration method is shown below.

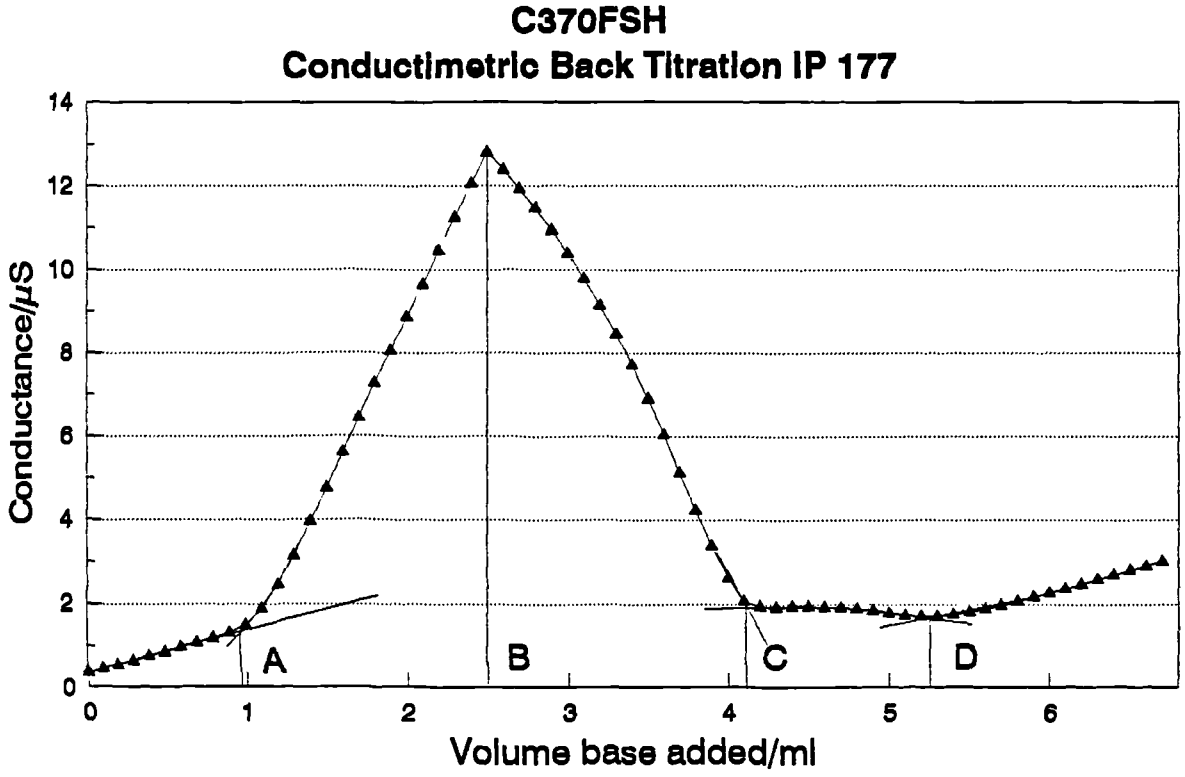


Figure 3.g

The volumes marked as A, B, C and D represent

A Volume of $HCl_{(alc)}$ added to neutralise basic constituents

B-A Volume of excess $HCl_{(alc)}$ added

C-B Volume of $KOH_{(alc)}$ added to neutralise excess $HCl_{(alc)}$

D-C Volume $KOH_{(alc)}$ required to reform original base constituents and neutralise acid components in oil

The region after D represents excess $KOH_{(alc)}$

When determining points A, B, C and D it was useful to remember that the number of moles of excess acid were equal to the number of moles of base required to neutralise the excess acid, B-A = C-B (moles).

$$m_{HCl} \times v_{HCl} = m_{KOH} \times v_{KOH}$$

where v_{HCl} represents region B-A
v_{KOH} represents region C-B
m_{HCl} = molarity of $HCl_{(alc)}$
m_{KOH} = molarity of $KOH_{(alc)}$

The Base and Acid Numbers were calculated using the following equations.

$$\textit{Base number} = \frac{m_{HCl} \times v_{HCl} \times 56.1}{mass_{oil}}$$

where m_{HCl} = molarity $HCl_{(alc)}$ mol dm^{-3}
v_{HCl} = volume $HCl_{(alc)}$ to point A

Acid Number = Apparent Acid Number - Base Number, where the apparent Acid Number is calculated as below.

$$\textit{Apparent acid number} = \frac{m_{KOH} \times v_{KOH} \times 56.1}{mass_{oil}}$$

where m_{KOH} = molarity $KOH_{(alc)}$ mol dm^{-3}
v_{KOH} = volume $KOH_{(alc)}$ from point C to point D

The Base and Acid Numbers were calculated for all the oil samples, the results are shown below.

Table 3.d

	Base Number/ mg KOH/g oil		Acid Number/ mg KOH/g oil	
Sample name	BN 1	BN 2	AN 1	AN
Q8LSREF	9.3	9.5	0.2	0.5
Q8TRZ	9.9	9.9	0	0.3
Q8SUMP	9.2	9.0	0.5	0.7
ETHFSH	9.6	9.2	-1.1	-0.8
ETHTRZ	8.5	8.6	2.7	4.0
ETHSUMP	8.8	8.7	-1.2	-0.9
DAAFSH	9.3	9.1	-0.3	-0.4
DAASUMP	7.3	6.9	0.3	0.3
ETH102E	9.1	8.8	0.7	0.6
C370FSH	7.6	7.5	0.3	0.3
C37036	7.4	7.0	-0.1	0.0
C37072	7.9	8.2	0	0.2
C370108	8.1	7.9	0.5	0.5
SAABEOT	2.5	2.4	1.4	1.2
SHELLFSH	6.5	6.5	0.4	0.6
SHELLSUMP	1.8	1.9	2.7	2.5
ETHNO6	1.8	2.0	2.5	2.2

3.5.4 Discussion

The conductimetric IP 276 Base Number results were found to be higher than the corresponding conductimetric IP 177 Base Number results, particularly for the severely degraded oils. The two bar charts below compare the different average

Base Numbers obtained by the two methods for both diesel and gasoline samples respectively.

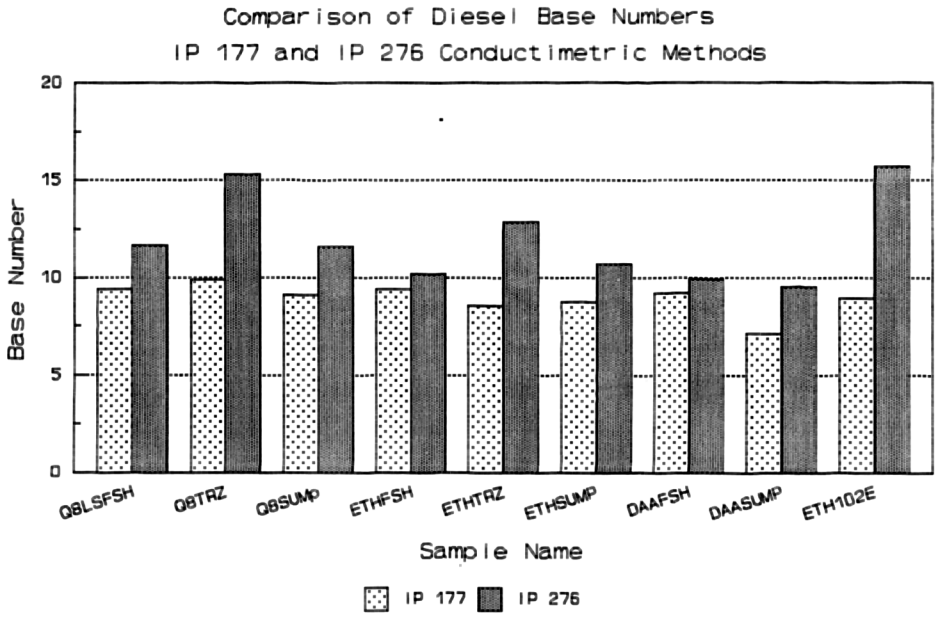


Figure 3.h

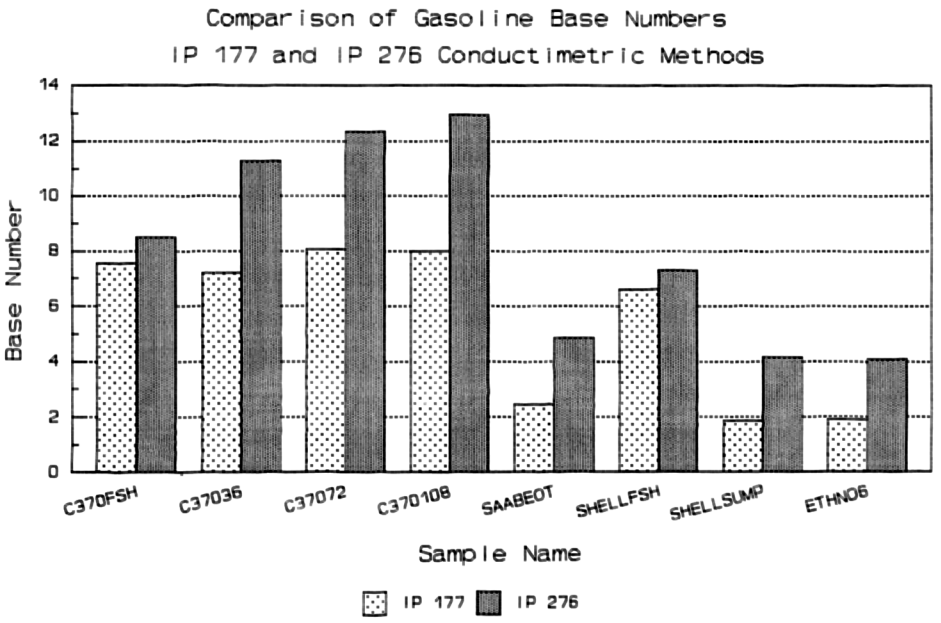


Figure 3.i

The results obtained using IP 276 were significantly higher than those obtained using IP 177.

Comparisons of the average Acid and Base Number results obtained using the conductimetric IP 177 back titration method have been made for both the diesel and gasoline samples, as shown in Figures 3j and 3k.

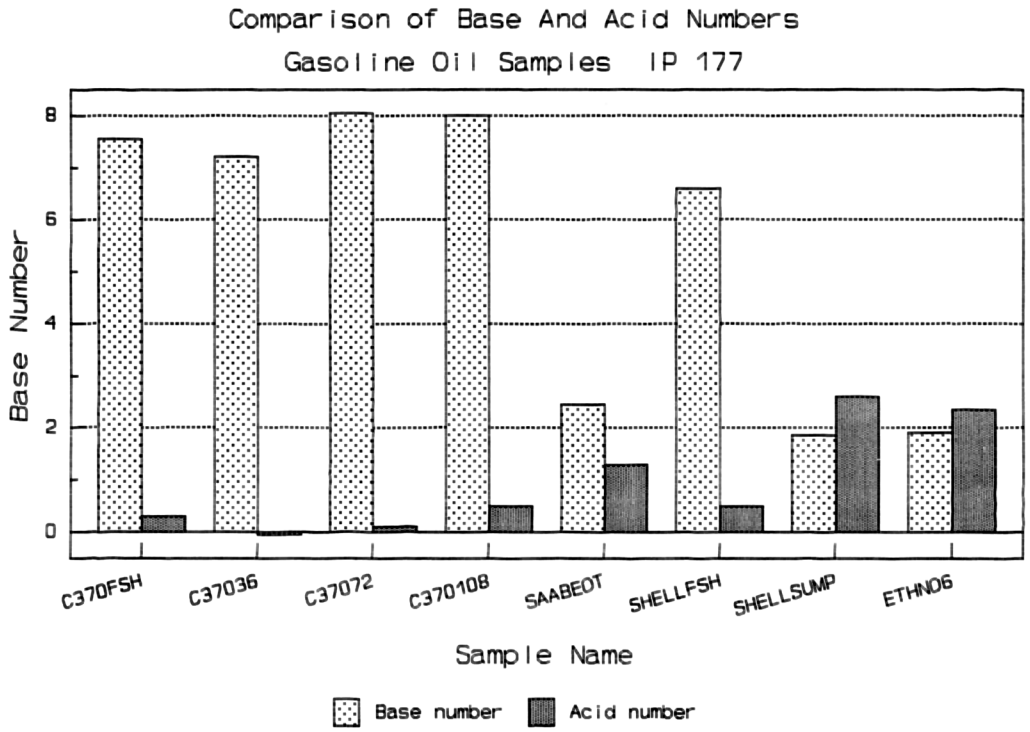


Figure 3.j

From the bar chart above it can be seen that the set of oils obtained from the Petter W1 at 36 hour intervals appear to have very similar Base Numbers. The relative volatility results showed that the oil volatility decreases as the duration of the engine test increases, indicating loss of base oil. Loss of base oil would result in an increase in both additive content and Base Number. The Base Number results obtained from the Petter W1 samples taken every 36 hours therefore indicated that the Base Number had in fact decreased with engine time.

The Base Number results must be compared together with the volatility results.

The Acid Number results show that the samples named SAABEOT, SHELLSUMP and ETHNO6 have significantly higher Acid Numbers than the remainder. From the relative volatility results it was seen that these samples were contaminated with low volatile components, probably fuel. It is therefore difficult to comment on the precise nature of the acidic components in the oil samples, especially as the Acid Number method has not been verified. The Base Numbers were particularly low for these samples, which corresponds with the high Acid Numbers.

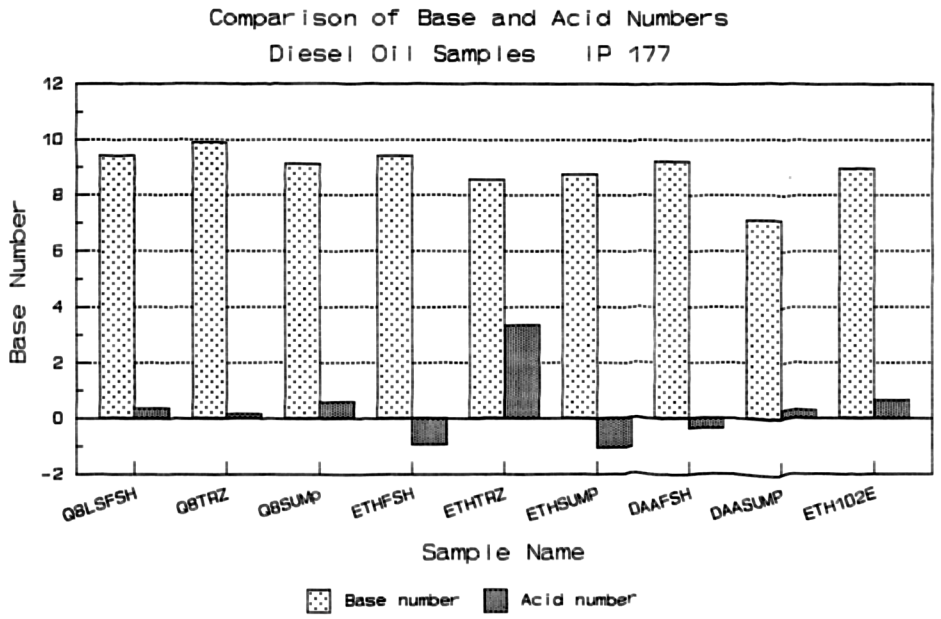


Figure 3.k

The diesel oil samples all seem to have Base Numbers around that typical of a fresh sample, DAASUMP being the exception with a significantly lower Base Number. The volatility results obtained from the used oils show that volatile loss has occurred, which would increase the Base Number. The Base Number for each used oil must therefore have decreased. The Acid Number results can be

seen to be just above zero or negative. The one exception is ETHTRZ, which has an average Acid Number of 3.4. The two results obtained for this oil were 2.7 and 4.0, the repeatability poor. Lack of sample prevented more analyses. Nevertheless the results indicated a relatively high Acid Number. The conductance trace obtained for Q8TRZ was particularly difficult to interpret, as shown in Figure 3.I.

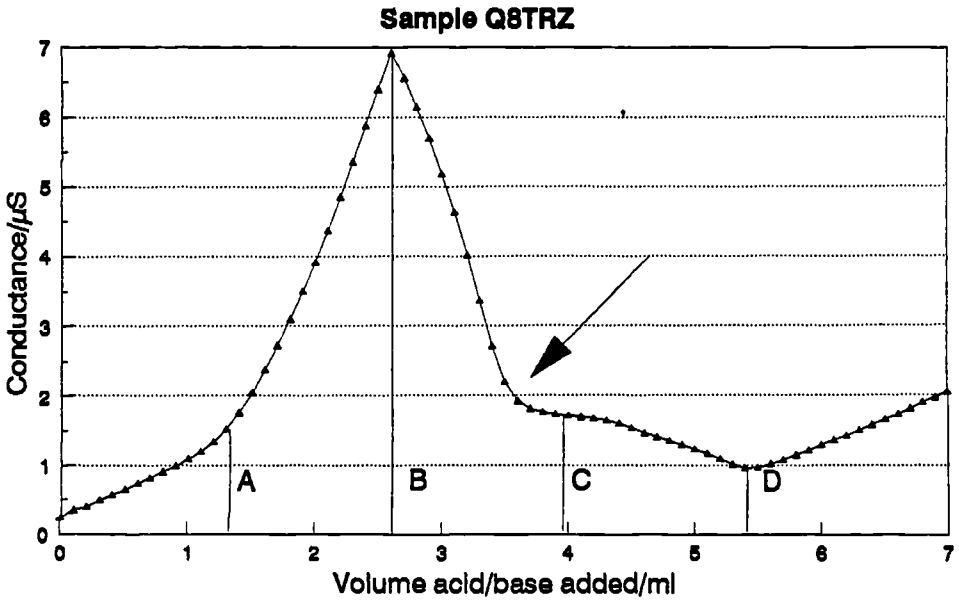


Figure 3.I

The point at which all the excess acid had been neutralised must be at point C and not as indicated by the arrow head, as might be expected. The number of moles of acid from A to B equal the number of moles of alkali from B to C. Moving point C to a lower value would in fact shift point A to a higher value, if the number of moles are to be kept equivalent. This problem was not encountered for other samples.

The Acid Number results for ETHFSH and ETHSUMP were found to be negative. These oils were also interesting as the final oil/solvent mixture for both was an

intense purple colour. Further investigation showed that the colour change occurred precisely as the conductance began to rise beyond point D. One of the components in the oil, presumably one of the additives present, was acting as a colour indicator, colourless in acid conditions and purple in alkali environment. The additive responsible for this phenomena was determined as discussed in 3.6.

3.5.5 Conclusion

The Base Number determination by conductimetric titration is a repeatable method which requires a small sample and is therefore well suited for the determination of top ring zone Base Numbers. The Acid Number results for the used oils were in some cases unexpected, for example negative results were obtained. The conductimetric Acid Number requires further development to assess both the repeatability and the reproducibility.

The results obtained for used oil samples from both methods can be misleading due to concentration effects. The results must therefore be compared together with volatility results.

3.6 Determination of Colour Indicator

As described above ETHFSH and ETHSUMP, and probably ETHTRZ, underwent a distinct colour change once the point of excess base was reached. Such an indicator could prove very useful in confirming the conductimetric Acid Number method. If the colour change was detectable for severely contaminated used oils using a spectrometric method of detection then there would be a possibility of a an alternative forward indicator titration method, avoiding the use of the conductance electrodes.

Ethyl Petroleum were very helpful in identifying which additive system was responsible for the colour change, the phenolic antioxidant. They provided a small sample which was then analysed by thin film infra-red analysis. The spectrum obtained for the additive is shown below, which matches the spectrum of a methylene bridged polyalkyl phenol, as shown in a book of spectra by Coates and Setti.

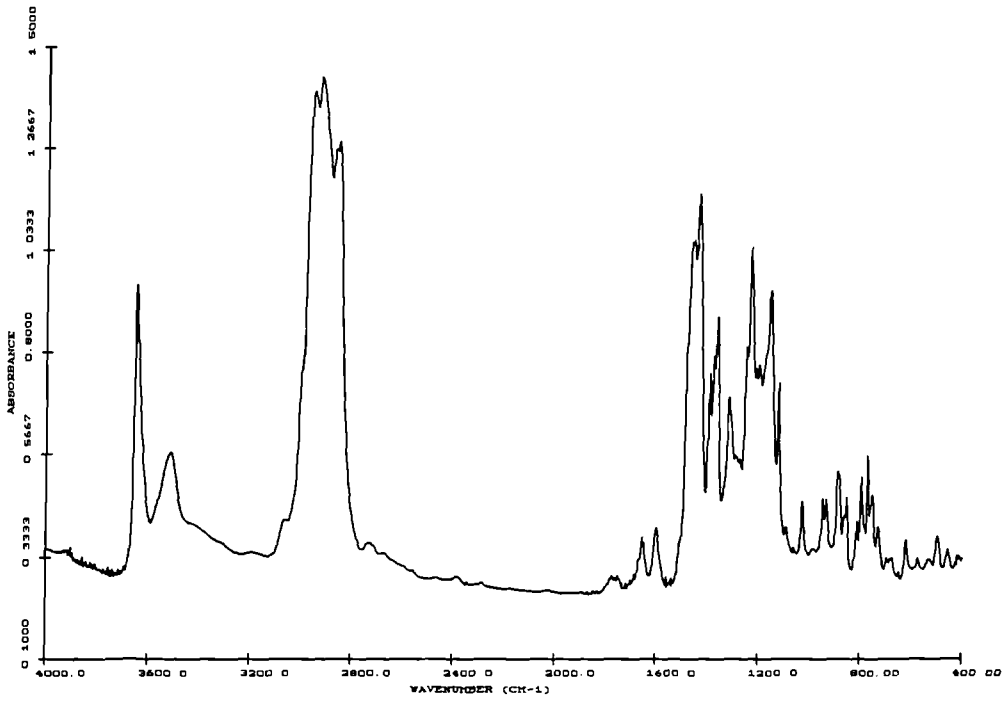


Figure 3.n

Unfortunately additives purchased from a manufacturer are not pure compounds, usually a mixture of similar, yet different, closely related compounds.

There is scope for a considerable amount of work to be carried out in determining the use of the phenolic additive as a colour indicator in an Acid Number determination method. A set of oils would be required of known Acid

Number values to develop a new Acid Number test method. This has proved to be difficult in the past.

Separation of the additive followed by a detailed analysis of the fractions would further clarify the phenolic structure.

CHAPTER 4 Infrared Analysis

4.1 Introduction

Infrared analysis is a well established analytical technique initially developed in the 1940's. It is used to detect and identify the characteristic vibrations of molecules. The energy of most molecular vibration corresponds to that of the infrared region of the electromagnetic spectrum, $3x10^{12}$ to $3x10^{14}$ Hz (100μm to 1μm), although the most useful vibrations occur in the narrower range 2.5μm to 16μm. The position of an absorption band in the spectrum may be expressed in terms of microns (μm) but is more commonly given as the reciprocal wavelength (cm^{-1}). The useful range is therefore $4000cm^{-1}$ to $400cm^{-1}$, possibly $200cm^{-1}$ according to the optics used.

As the infrared radiation passes through a sample, energy is selectively absorbed corresponding to the vibration of specific chemical bonds. A plot of absorbance versus wavenumber gives a pattern which is like a "finger print" for a sample, the infrared spectrum. Comparison of spectra enables the identification of particular functional groups. Fortunately, the position of an absorbance due to a particular functional group does not significantly change from one sample to another. The infrared spectrum of a sample is obtained by an infrared spectrometer, consisting of a source of infrared light, which emits radiation throughout the whole frequency range of the instrument. The radiation is split into two beams of equal intensity, one of which passes through the sample. Energy is absorbed by the sample at frequencies coinciding with that of a particular vibration within the sample. The spectrum is obtained by comparing the intensity of the two beams after one has passed through the sample. The wavelength range over which the comparison is made is spread out with a prism or grating.

More recently a new method is used to obtain an infrared spectrum, called Fourier Transform Infrared Spectroscopy, FTIR. The infrared light is split into two

beams as before. Either one beam is passed through the sample, or both are passed, but one beam is made to travel a longer path than the other. Recombination of the two beams produces an interference pattern that is the sum of all the interference patterns created by each wavelength in the beam. By systematically changing the difference in the two paths, the interference pattern to produce a detected signal varying with optical path difference. This pattern is the interferogram, which looks nothing like a spectrum. Fourier transform of the interferogram using a computer converts it into a plot of absorbance against wavenumber which is then a traditional spectrum. One of the major advantages of this method is that it is not necessary to scan each wavenumber individually, for the whole spectrum is measured in a few seconds rather than minutes, known as the Fellgett advantage [16]. Once the spectra are saved onto disc it is very easy to subtract spectra from each other at any future time.

Infrared analysis is probably the technique which is most frequently used in the analysis of oils and their components. It was first used for identifying and estimating lubricating oil additives in the late 1940's. An early paper in 1952 [17] describes the type of problems that were solved using IR and the need of the Air Force for accumulated compositional data. Powell and Evans [18] described the use of a variable thickness cell highlighting the benefits of quantitative work with reference to some hydrocarbons. The interference fringes produced from a blank cell were used to calculate the thickness of the cell from the following relationship.

$$t = \frac{n \times \lambda_1 \lambda_2}{2 \times (\lambda_1 - \lambda_2)}$$

where t = cell thickness (m)

n = number of maxima (or minima) observed between wavelengths λ_1 and λ_2 (m)

In 1956 Powell [19] discussed the application of differential infrared spectrometry as applied to the analysis of petroleum products. Infrared analysis rapidly became popular particularly with the introduction of modern, low cost, easy to use spectrometers. The direct comparison of used oil samples with fresh oil permitted the quantitative measurement of both additive depletion and contamination build-up. This was useful when analysing the condition of oils in service, the application of which was discussed in the 1960's [20-22]. As lubricating oils became more complex in composition due to the ever increasing performance demands of the internal combustion engine, so too did the interpretation of spectra become more complex. A review of used engine oil analysis in 1977 [23] emphasised the difficulties encountered. As an example the absorbance around 1720 cm^{-1} can be an indication of oil oxidation or the presence of certain viscosity index improvers or dispersants.

The analysis of lubricants became significantly more sophisticated with the advent of the computer. In 1983 a "State of the art" system was reported by Lawrence et al [24] which used a computer to control a sampling valve to transfer an oil sample from a test engine to an infrared cell. The sample was analysed and returned to the engine. The so called on-line computer assisted infrared spectroscopic technique measured concentrations of additives and oxidation components as well as the spectrum whilst the engine ran. The concentrations were plotted against time as the engine was running.

In the mid 1980's Coates and Setti published several papers based on the infrared analysis of used oils describing the condition monitoring of crankcase oils using computer aided IR spectroscopy [25], the analytical and statistical evaluation of IR data from used Diesel lubricants [26], infrared spectroscopy as a tool for monitoring oil degradation [27] and IR spectroscopic methods for the study of lubricant oxidation products [28]. The IR analysis of heavy-duty Diesel engine oils was reported by Wooton et al [29] in 1984. Characteristic absorbance bands determined from the spectra of used oils are as follows;

Wavenumber/cm^{-1}	Description
2850-3000	hydrocarbon, saturated C-H stretching
3000-3100	hydrocarbon, alkene and aromatic C-H stretching
1370-1470	hydrocarbon, saturated C-H bending
720	hydrocarbon, saturated C-H rocking
3650-3590	free -OH, sharp, stretching
3200-3600	H-bonded OH, broad
3100-3500	N-H stretching
1665-1800	carbonyl oxidation C=O, eg esters, lactones, ketones, aldehyde
1585-1620	carboxylate salt
1650-1620	nitrate ester, $RONO_2$
1570-1540, 1290-1270	nitro-oxidation, RNOx
1200-1130	C-O-C oxidation
1150, 600	sulphate

Other absorbances due to additives present within the oil can include:

Wavenumber/cm^{-1}	Description
1720-1750	ester carbonyl
1725-1700	acid carbonyl
1710-1700	imide
1680-1620	amide
1500-1380, 870-850	carbonate
1230-1120, 1080-1025	sulphonate
1000-970	ZDDP, P-O-C
750-600	ZDDP, P=S

As can be seen many absorbances overlap each other and great caution must be taken when interpreting infrared spectra. It is important to note that this type of analysis, exemplified by Coates and Setti assumes a constant volume of oil, ie, only the components have changed in an unchanged total volume.

Characterisation of both fresh and used oil components can be simplified by separating the oil samples prior to analysis. A method which separates the species present within the oil according to their approximate molecular weight is known as dialysis. The dialysis of petroleum products was reported by Hill and Munsell in 1960 [30]. A thin walled rubber sac, "medical fingercot", was used as the dialysis membrane. A soxhlet extractor, together with condenser, 500ml round bottomed flask and heating mantle, was used to continuously circulate a low boiling paraffinic hydrocarbon around the rubber sac. The top of the 'U' bend of the syphon tube of the Soxhlet extractor was enlarged so that the solvent overflowed continuously rather than syphoning periodically. The oil sample, approximately 8-10g, was refluxed overnight allowing material to diffuse through the membrane wall and collect in the flask, the dialysate, residue remaining within the rubber sac. After dialysis the solvent was removed from both the dialysate and residue and analysed using infrared spectroscopy. The application of dialysis for the separation of a variety of petroleum products was reported by Hill and Munsell [30], both qualitative and quantitative studies. Lubricating oil additives, for example, were combined into a mixture of known composition and then dialysed into the following fractions, as determined by infrared analysis.

Dialysate (68.6%)	Dialysate Residue (31.4%)
Base oil	Metal dialkyldithiophosphate
Metal dialkyldithiophosphate	P_2S_5 treated polybutene
P_2S_5 treated polybutene	Metal sulphonate
Alkylated phenol	Metal carbonate
	Metal alkylated phenate

A used motor oil was dialysed to give a black gum residue (9%) and a clear, deep red oil dialysate (91%). No information was given regarding the chemical composition of the two fractions.

The method was found to be a simple and effective way to separate petroleum products. The analysis of lubricant and additive concentrates using spectroscopy and physical methods of separation was later discussed by Jenkins and Humphreys [31] in 1964. They used toy white balloons as the dialysis membrane although different rubber membranes were tried such as fingercots, black gloves and inner tube. The latter were found to be no better than the toy balloons. The samples, 19 oil additives, were individually placed in a balloon with 100ml pet ether and then immersed in 1500ml of the same solvent. After 24 hours the solvent was removed from the dialysate and residue. They did not use a soxhlet extractor arrangement as described by Hill and Munsell [30]. Alkyl borates, alkyl aryl phosphates, low molecular weight esters, hindered phenols, zinc dithiocarbamates and zinc dialyldithiophosphates were found to diffuse readily through the toy balloon. The high molecular additives did not diffuse through the membrane wall. These results were consistent with previous work. A series of papers were published in the Khimiya i Technologiya Topliv i Masel from 1968-1988 describing the use of dialysis in the separation of alkylphenol additives [32], the separation of alkylsalicylate and sulphonate additives by dialysis [33], the repeatability of additive dialysis [34], factors effecting dialysis (solvent, type of membrane, sample size) [35], the kinetics of dialysis [36] and the dialysis of dialykldithiophosphates in combination with dispersant/detergent type additives [37]. From these papers the following conclusions were made:

1) Individual pure low molecular weight components diffuse to completion according to first order kinetics.

2) The dialysis of additive mixtures can become more complicated due the interaction between additive components.

3) The membrane type, solvent, dialysis time and temperature must be consistent if results are to be compared.

The use of dialysis appears to be primarily concerned with the separation of fresh oil and additive samples. Used oils, particularly diesel samples, contain a significant amount of particulates, soot, which could possibly interfere with the membrane separation. The technique was nevertheless considered to be a valid method for comparing the samples in this work. The oxidation products which diffuse through the membrane wall should be separated from the high molecular weight additives, which can interfere with the interpretation of infrared spectra.

Another technique for separating oil and additive samples involves the well established method of liquid phase chromatography. This technique separates the components according to their polarity, as opposed to their size. This method was used by Jenkins and Humphreys [31], as well as dialysis. A column 2ft x ¾ inch was filled to a depth of 6 inches with activated 100-200 mesh silica gel. A 10g sample was dissolved in 100ml pet ether and passed through the column, and the column then desorbed with ether. Low molecular weight polar additives were retained on the column, while high molecular materials, detergent additives and most of the oil were reported to have passed through. Variations in the procedure included the use of benzene and methanol to obtain additional fractions and the use of longer silica columns. Other similar techniques have been developed over the years making use of different solid phase materials and different solvents. As silica gel is cheap and readily available it was decided to separate the oil samples using liquid chromatography into two fractions, polar and non-polar.

The set of oil samples analysed were those previously mentioned in Chapters 2 and 3, consisting of both fresh and used diesel and gasoline samples. The neat samples were analysed initially by infrared spectroscopy followed by the analysis of those which had been separated into simpler fractions. The set of oil samples

are listed below, the diesel samples followed by the gasoline samples:

Sample Name	Description - diesel oils
Q8LSREF	Fresh diesel multigrade oil supplied by Kuwait Pet.
Q8TRZ	Q8LSREF run in Petter AA1, top ring zone sample
Q8SUMP	Q8LSREF run in Petter AA1, sump sample
ETHFSH	Fresh diesel oil supplied by Ethyl Pet.
ETHTRZ	ETHTRZ run in Petter AA1, top ring zone sample
ETHSUMP	ETHTRZ run in Petter AA1, sump sample
DAAFSH	Fresh diesel oil
DAASUMP	Above oil taken from Peugeot 405 car after 10 000 miles
ETH102E	End of engine test diesel oil supplied by Ethyl Pet.

Sample Name	Description - gasoline oils
C370FSH	Fresh gasoline multigrade oil supplied by Castrol
C37036	Sample taken from sump of Petter W1 engine test after 36 hrs, fresh oil C370FSH
C37072	Sample taken from sump of Petter W1 engine test after 72 hrs, fresh oil C370FSH
C370108	Sample taken from sump of Petter W1 engine test after 108 hrs, fresh oil C370FSH
SAABEOT	End of SAAB engine test, fresh oil C370FSH
SHELLFSH	Shell gasoline multigrade, as bought from shop
SHELLSUMP	Above oil taken from sump of Ford Escort after 6 000 miles
ETHNO6	End of engine test oil supplied by Ethyl

4.2 Experimental Method

4.2.1 Infrared Analysis

A Nicolet 5DXR Fourier Transform Infrared Spectrometer with a resolution of 4cm^{-1} was used for the analysis of fresh and used oil samples. A zinc selenide (ZnSe) fixed path length cell (0.1mm) was used as opposed to a potassium bromide (KBr) cell as some of the additive fractions lead to rapid deterioration of the KBr plates. The interference fringes produced by the ZnSe cell caused problems with the baseline of the spectra. This was rectified by tilting the cell at approximately 45° using a device designed and made at De Montfort University. The angle at which the cell was held remained constant for all the analyses. A simplified diagram is shown Figure 4.a.

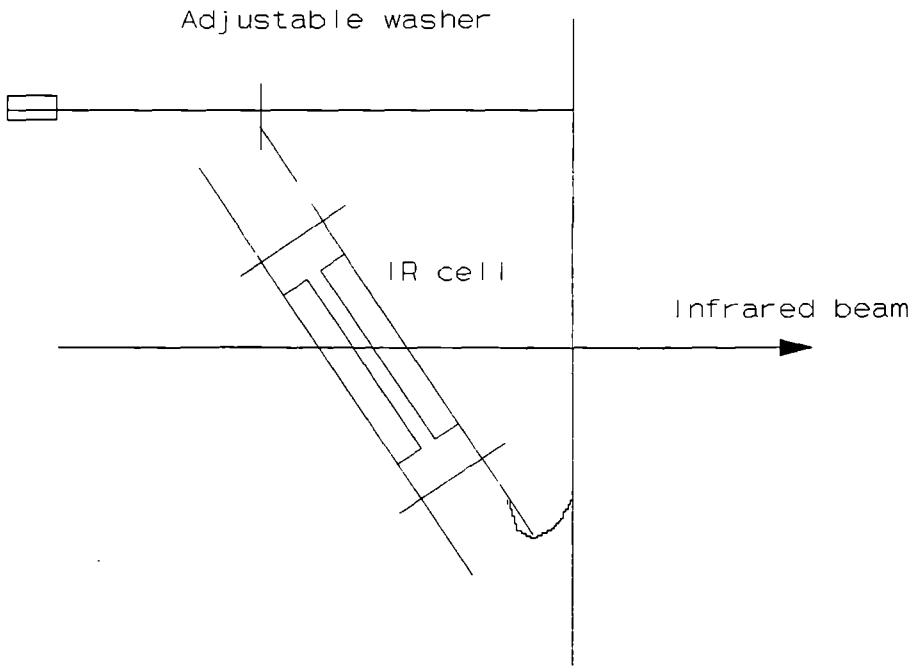


Figure 4.a

A background spectrum was first taken using the clean empty cell. The sample was carefully placed into the cell using a pasteur pipette avoiding the admission of air bubbles. The infrared spectrum was recorded and saved onto a floppy disc. Once the sample had been removed the cell was thoroughly cleaned with dry hydrocarbon and acetone. A background spectrum was then taken as before and the process repeated with a different sample. All the samples were analysed as described.

4.2.2 Dialysis

A Regent X200-906 medical fingercot was used as the dialysis membrane. The oil sample, 3g, was placed in the fingercot recording the weight of oil. The fingercot was then lowered into the Soxhlet extractor containing pentane and left overnight suspended in the solvent. The following morning the heating mantle was switched on and allowed to reflux for 7 hours. The contents of the flask contained the dialysate and solvent whereas the fingercot contained residue and pentane. The solvent was removed from both fractions to constant weight. A small amount of tetracosane, a relatively non-volatile hydrocarbon solvent, 0.5ml was then added to the residue, as the sample was otherwise too viscous to place into a 0.1mm cell. Both fractions were then analysed using infrared spectroscopy. Initially sample ETHFSH was dialysed repeatedly to give an indication of the repeatability of the method. All the other samples were then dialysed.

The arrangement of the apparatus as described is shown in Figure 4.b.

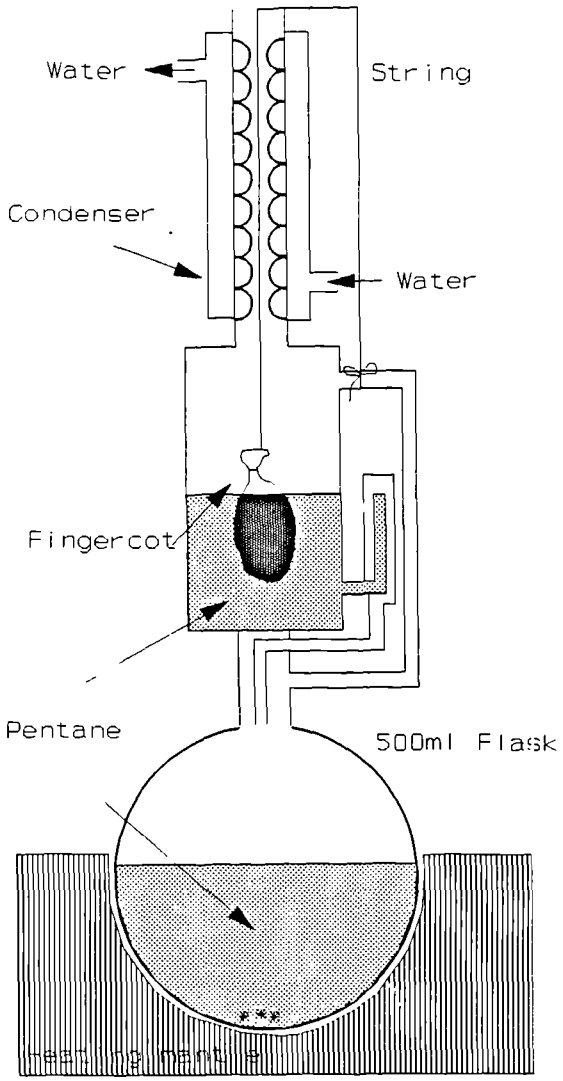


Figure 4.b

4.2.3 Liquid Phase Chromatography

Based on conventional liquid phase flash chromatography, the sample mass is usually approximately 2% of the silica gel used, ie.

$$\frac{Mass\ sample}{Mass\ silica\ gel} \times 100 = 2\%$$

Automotive lubricating oils however contain approximately 90% of non-polar material which should not be retained on the silica gel. The amount of oil loaded onto the silica gel was therefore based on the following relationship:

$$\frac{Mass\ oil\ sample}{Mass\ silica\ gel} \times 100 = 20\%$$

A weighed amount of silica gel was shaken in a large pyrex beaker together with pentane to form a slurry. The slurry was then poured into the glass column and allowed to settle. Slight suction was applied to bring the solvent level down to that of the silica gel surface. The oil sample was diluted with pentane and carefully loaded onto the silica surface with as little disturbance as possible. The sample was drawn just below the surface and then eluted with pentane. Before the polar components remaining on the column were removed using methanol, the column was dried using suction. Two fractions were collected, the base oil fraction, eluted with pentane and the additive fraction, eluted with methanol. The solvents from both fractions were removed using a rotary evaporator. The resulting samples were then analysed using infrared spectroscopy. Initially experiments were based on the oil sample ETHFSH to assess the potential of the method. The results, as given later, were not very satisfactory. The remaining oil samples were not therefore separated using this method.

The apparatus used for the separations is shown below in Figure 4.c.

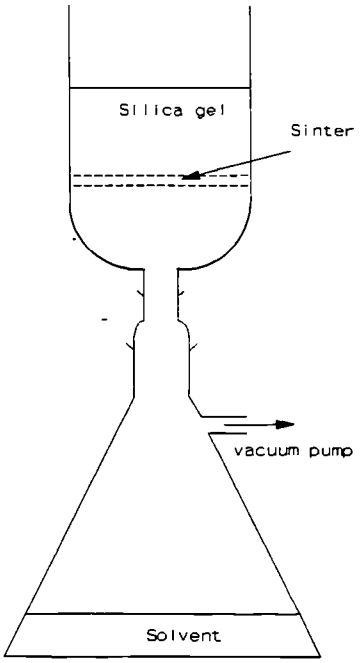


Figure 4.c

4.3 Results and Discussion

4.3.1 Infrared Analysis of Neat Samples

Diesel Oil Spectra

The infrared spectra of all the diesel samples are shown below except the end of engine test oil named ETH102E, supplied by Ethyl Pet. This oil was found to contain a very high particulate content resulting in a very poor infrared spectrum. Figure 4.d compares the infrared spectra obtained from the fresh, sump and top ring zone samples named Q8LSREF, Q8SUMP and Q8TRZ respectively.

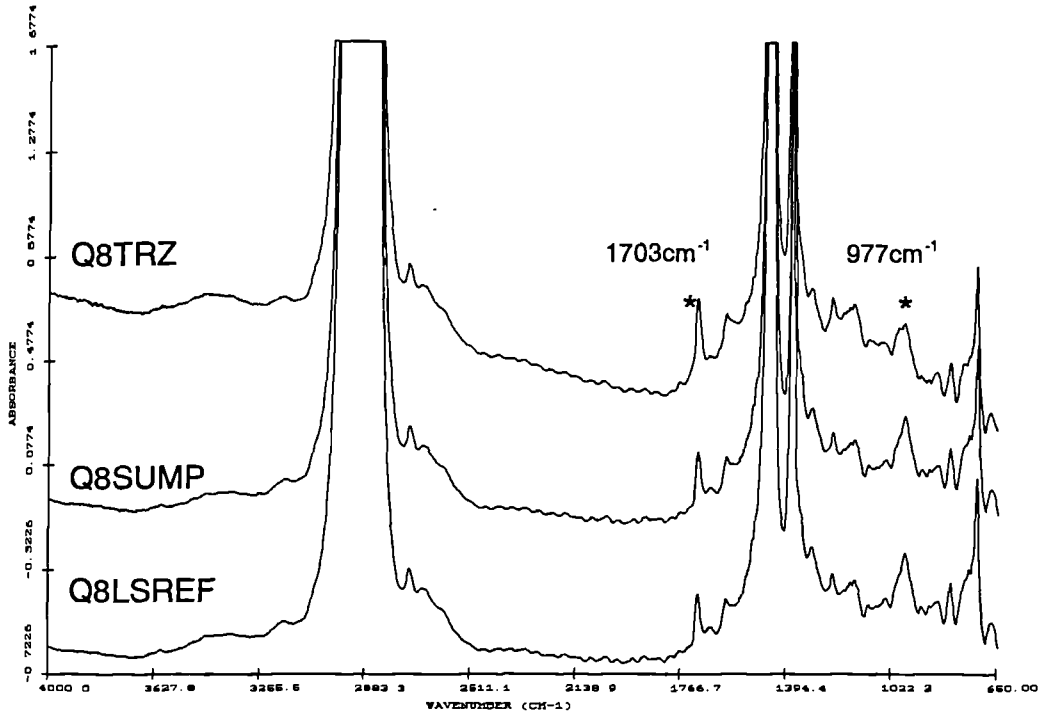


Figure 4.d

The presence of soot and other dispersed insolubles is readily observed in the comparison of used and fresh diesel oils. The characteristic baseline slope can be seen above, in the top ring zone spectra. The effect is caused by light absorption and scattering. The intensity of the peak at 1703 cm^{-1}, assigned to the polyisobutenyl succinimide (PIB succ.) is visually greater for the top ring zone sample, compared with the sump and fresh oils. The increase in intensity results from additive concentration, presence of carbonyl oxidative products, or a combination of the two. The intensity of the peak at 977cm^{-1}, assigned to a zinc dithiodialkyl phosphate (ZDDP), is noticeably smaller in the top ring zone spectrum.

Figure 4.e compares the infrared spectra obtained from samples ETHFSH, ETHSUMP and ETHTRZ. They are very similar to those shown above, which is not surprising as both fresh oils were run in the Petter AA1 diesel engine at

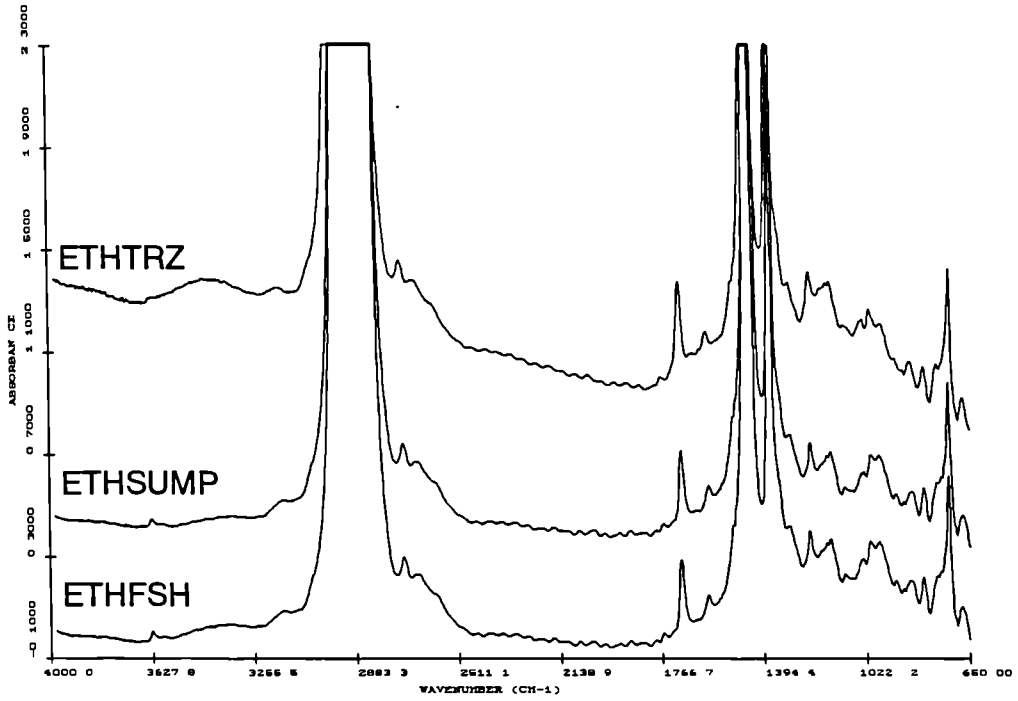

ETHTRZ
ETHSUMP
ETHFSH
ABSORBANCE
2 3000
1 9000
1 6000
1 1000
0 7000
0 3000
-0 1000
4000 0
3627 8
3255 5
2883 3
2511 1
2138 9
1766 7
1394 4
1022 2
650 00
WAVENUMBER (CM-1)

Figure 4.e

Figure 4.f compares the fresh and sump oil samples named DAAFSH and DAASUMP respectively.

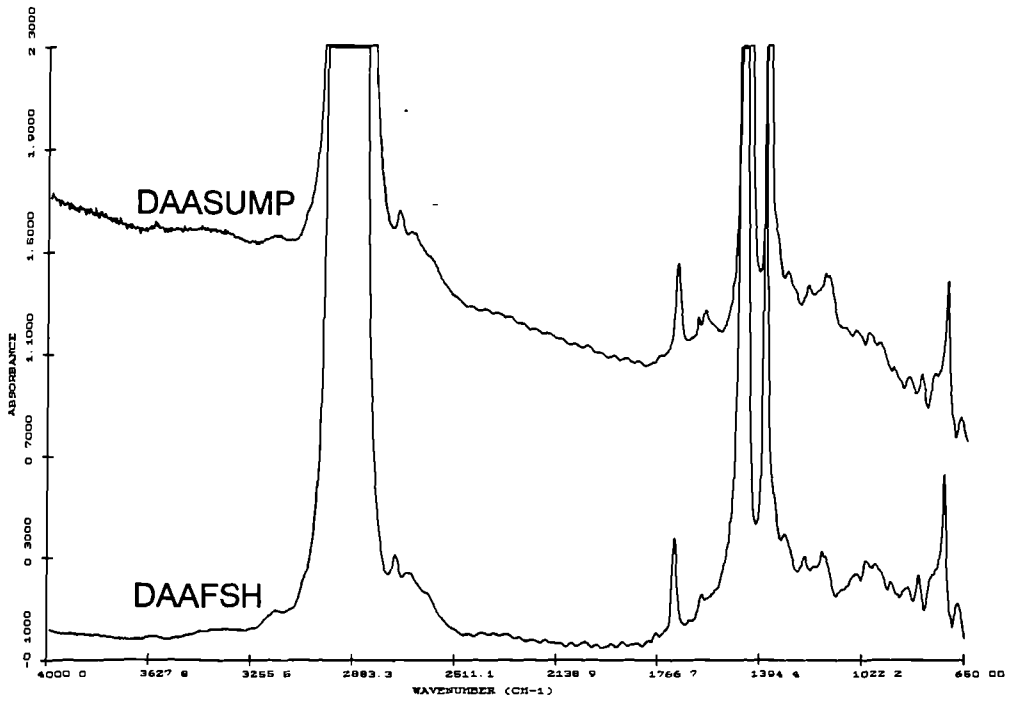


Figure 4.f

The slope of the baseline indicates a high particulate content for DAASUMP. An additional peak is observed in the sump oil spectra around 1600cm^{-1} assigned to a nitration product.

Gasoline Oil Spectra

All the infrared spectra obtained from the gasoline oil samples are shown below.

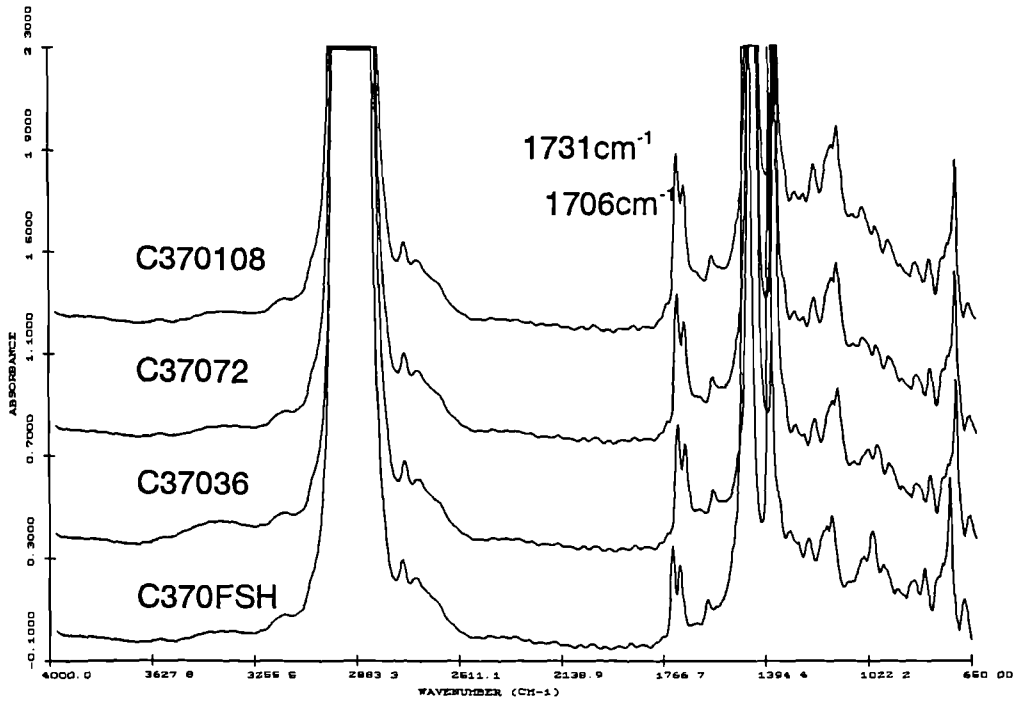


Figure 4.g

The two sharp carbonyl peaks at 1731cm^{-1} and 1706cm^{-1} were assigned to an ester-based viscosity index improver (VII) and PIB succinimide dispersant respectively. A gradual increase in absorption in this region can be seen for each sample in the series. As previously mentioned, the increase could be due to additive concentration due to base oil evaporative loss or oxidative degradation of the oil.

Figure 4.h compares the infrared spectra of ETHNO6, SAABEOT and C370FSH.

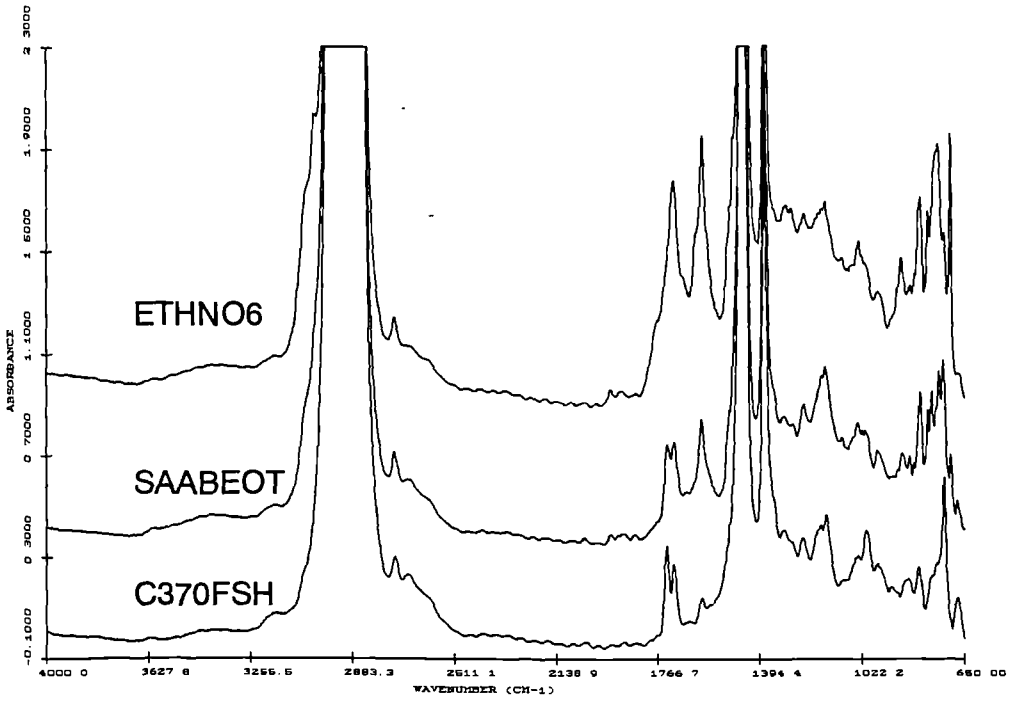


Figure 4.h

The infrared spectra of samples ETHNO6 and SAABEOT show strong absorption around 1600cm^{-1}, initially thought to be primarily due to nitration type products. Both these spectra also show an increases in absorption towards the lower end of the spectrum, characteristic of fuel dilution. The peak at 1731cm^{-1}, previously assigned to the ester VII is less apparent in the SAABEOT spectrum. Examination of the ETHNO6 spectrum shows a dramatic increase in absorption in the assigned carbonyl region.

Figure 4i, shown below compares the spectra of samples SHELLFSH and SHELLSUMP.

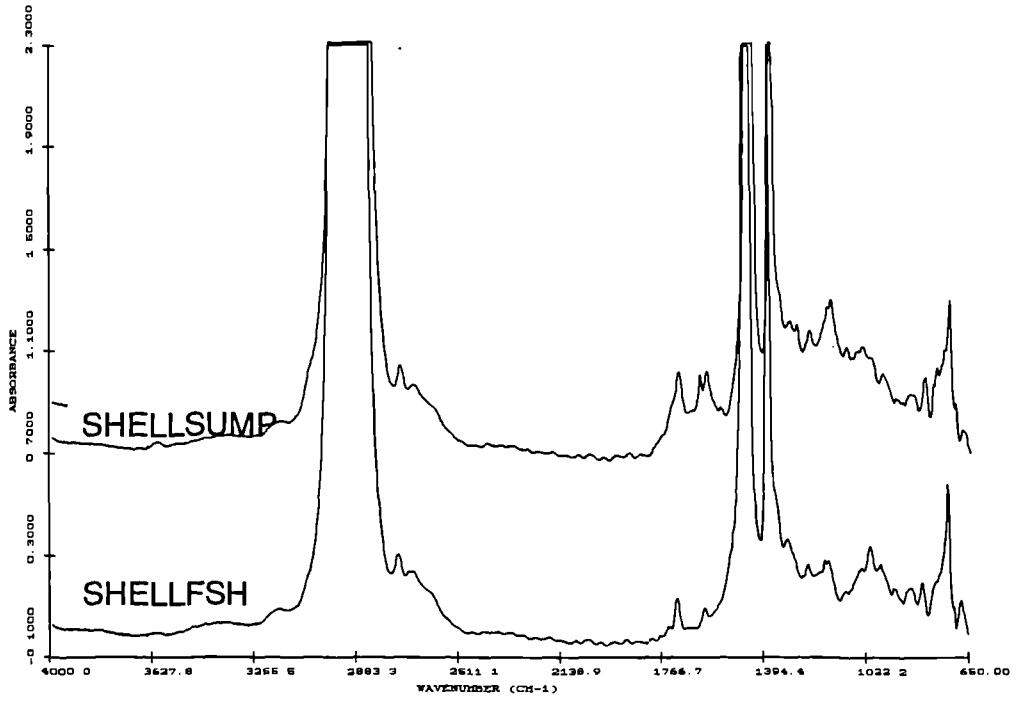


Figure 4.i

The spectra of the sump oil shows an increase in absorption in both the carbonyl and nitration regions. The peak at 1160cm^{-1} has also increased which could be due to C-O-C oxidation or sulphate formation.

Generally, the species that change most rapidly occur between approximately 1800cm^{-1} and 1500cm^{-1} and these are principally assigned to carbonyl compounds with nitrated species also occurring towards the end of the range. It is important to note however that there is a possibility of additive concentration which would also result in an increase in absorption in this region.

4.3.2 Infrared Analysis of Dialysed Samples

The dialysate and residue sample masses were recorded for each of the oil samples dialysed. The initial mass for all the samples was 3g, except ETHTRZ which was approximately 1.1g.

Table 4.a

Sample Name	Dialysate/g	Dialysis Residue/g
ETHFSH	2.91	0.19
ETHFSH	2.79	0.19
ETHFSH	2.85	0.20
ETHFSH	2.78	0.21
ETHFSH	2.8	0.21
ETHFSH	2.94	0.19
Q8LSREF	2.83	0.20
Q8TRZ	2.56	0.3
Q8SUMP	2.8	0.2
ETHTRZ	1.04	0.12
ETHSUMP	2.94	0.22
DAAFSH	2.83	0.2
DAASUMP	2.75	0.3
ETH102E	2.50	0.47
C370FSH	2.80	0.21
C37036	2.69	0.18
C37072	2.87	0.31
C370108	2.64	0.38
SAABEOT	2.66	0.21
SHELLFSH	2.88	0.11
SHELLSUMP	2.81	0.19
ETHNO6	2.65	0.35

The dialysate and residue samples collected from the repeated dialysis of ETHFSH have been compared by calculating the mean and standard deviation as shown below.

Dialysate/g

$$n=6 \quad \bar{x}=2.85 \quad \sigma_{n-1}=0.067 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=2.4 \quad =\%RSD$$

$$\therefore \textit{Dialysate} = 2.85 \pm 0.13 \ g$$

Dialysis Residue/g

$$n=6 \quad \bar{x}=0.20 \quad \sigma_{n-1}=0.010 \quad \frac{\sigma_{n-1}}{\bar{x}}\times 100=5.0 \quad =\%RSD$$

$$\therefore \textit{Residue} = 0.20 \pm 0.02 \ g$$

Based on the dialysate and residue masses alone the repeatability of the dialysis was good.

The fresh and used dialysate samples were easily analysed using the Nicolet spectrometer described earlier. The residue samples however were found to be more difficult to analyse as they required preliminary dilution as mentioned in the experimental. The residue samples from used oils containing high levels of soot could not be analysed by IR spectroscopy due to the light scattering and absorption caused by the concentration of soot and other insolubles.

The difference between the dialysate and residue samples obtained from the dialysis of ETHFSH can be seen in Figure 4j.

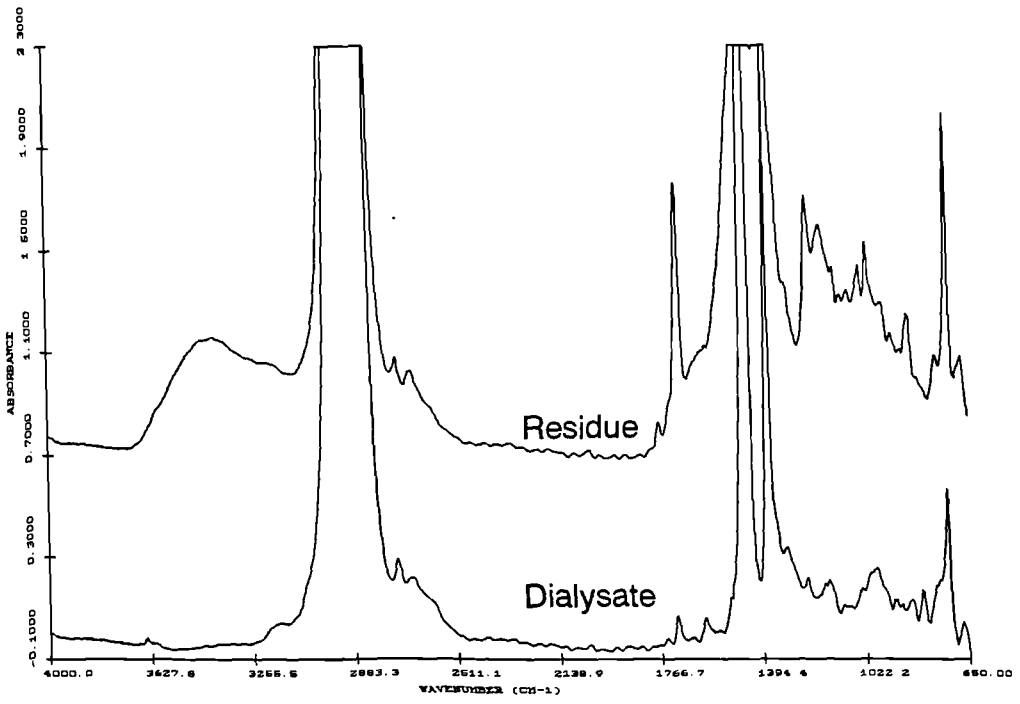


Figure 4.j

The high molecular weight components, for example the PIB succinimide, remain in the residue fraction whilst the low molecular weight additives, for example the phenolic antioxidant, diffuse through the membrane into the dialysate. The separation between low and high molecular weight components is not perfect however as shown in Figure 4.k, which shows the same dialysate spectra on a larger scale. The region marked X shows peaks assigned to the PIB succinimide, and region Y shows absorption due to aromatic rings. The aromatic ring content could be due to both base oil and additives in the blended oil.

The intensity of these regions can be quantified by integrating the peak areas using software available with the Nicolet spectrometer, which can integrate an area between two specified wavenumbers. The integral regions marked X (carbonyl region) and Y (aromatic ring) were determined for each of the dialysates obtained from the dialysis of ETHFSH.

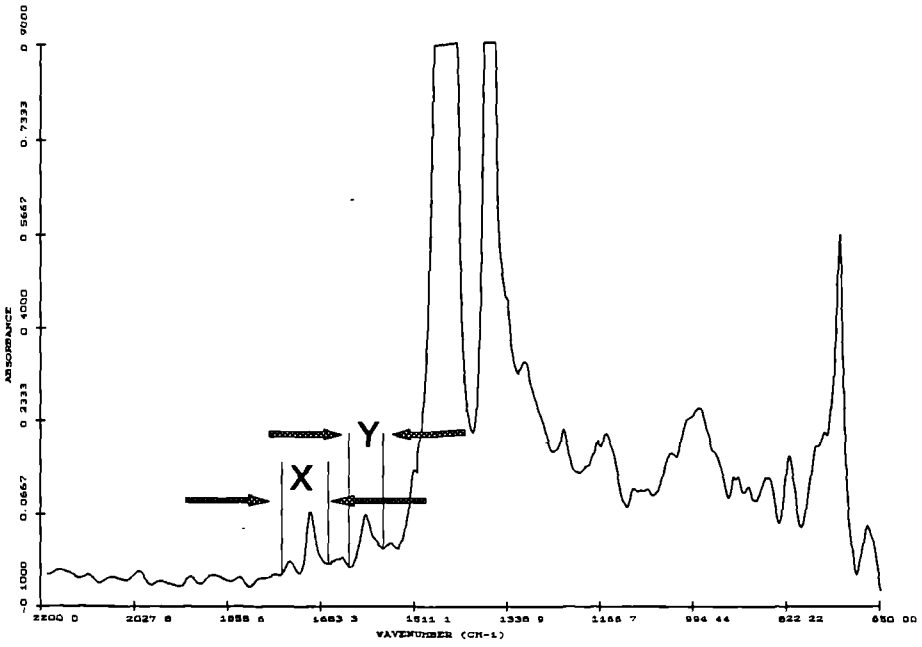


Figure 4k

Table 4.b Sample ETHFSH

	Region X	Region Y
1	2.3389	1.7566
2	2.2346	1.9198
3	2.2712	1.9445
4	2.0730	1.8630
5	2.1476	1.9038
6	2.3752	1.6182

The differences between each dialysis have been estimated by comparing the mean and standard deviations for both the dialysate regions.

Region X

$$n=6 \quad \bar{x}=2.24 \quad \sigma_{n-1}=0.11 \quad \frac{\sigma_{n-1}}{\bar{x}} \times 100 = 5.11$$

$$\textit{Region X} = 2.24 \pm 0.22$$

Region Y

$$n=6 \quad \bar{x}=1.83 \quad \sigma_{n-1}=0.12 \quad \frac{\sigma_{n-1}}{\bar{x}} \times 100 = 6.80$$

$$\textit{Region Y} = 1.83 \pm 0.24$$

If the oxidation products of a used oil pass through the membrane wall during dialysis an increase in absorbance in regions X and Y would be observed. The infrared spectra for the dialysates obtained from the dialysis of C370FSH and C370108 are shown in Figure 4.I.

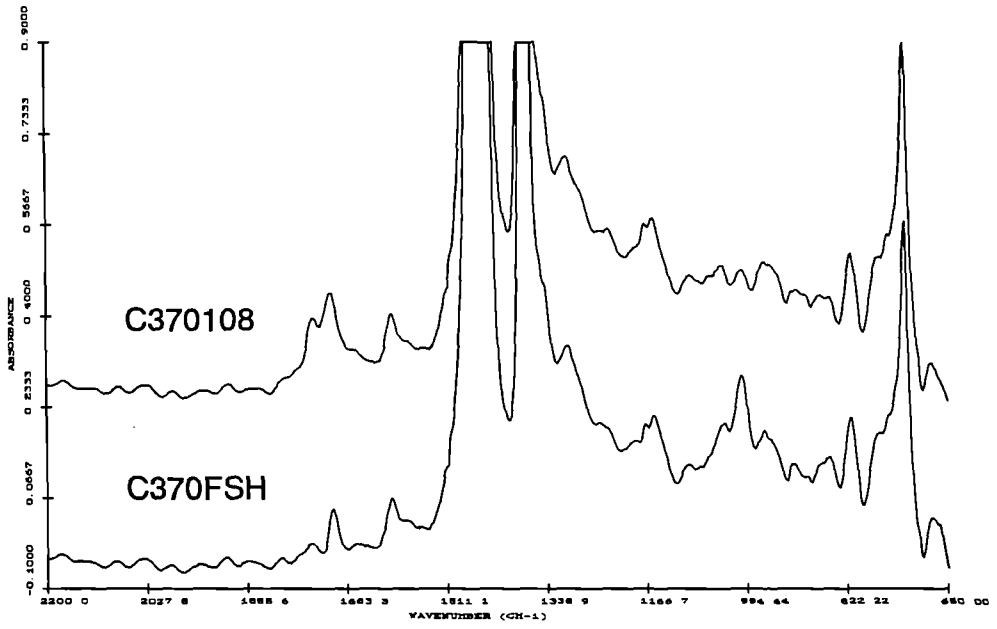


Figure 4.I

It can be seen that oxidation products are present within the C370108 dialysate. By subtracting the integral regions X and Y calculated from the fresh dialysate infrared spectra from those of the used oil dialysate gives a measure of the oxidation, as shown below.

	Region X	Region Y
C370108 dialysate	5.1	2.0
Fresh dialysate	2.2	2.0
Difference	2.9 ± 0.44	0 ± 0.48

The dialysate obtained from the dialysis of the used diesel sample ETH102E was easy to analyse by IR spectroscopy as the high particulate content remained in the residue fraction. The IR spectrum is shown below for the dialysate. (The IR spectrum of the neat oil sample was impossible to interpret due to the high soot content).

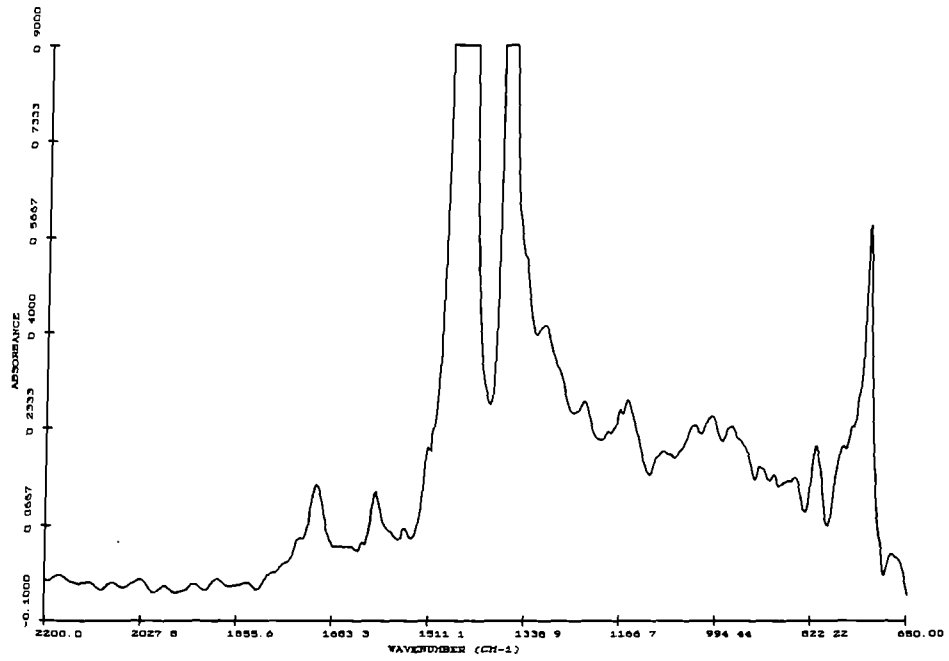


Figure 4.m

As the corresponding fresh oil was unavailable the regions X and Y were compared with those obtained from ETH001, a fresh diesel oil.

	Region X	Region Y
ETH102E dialysate	5.0	2.3
Fresh dialysate	2.2	1.8
Difference	2.8 ± 0.44	0.5 ± 0.48

The integral regions X and Y for all the dialysates and are given in Table 4.c.

Table 4.c

Sample name	Region X	Region Y
Q8LSREF	1.06	2.37
Q8TRZ	2.11	2.35
Q8SUMP	1.07	2.31
ETHFSH	2.24	1.83
ETHTRZ	2.62	2.17
ETHSUMP	2.07	1.81
DAAFSH	2.35	1.76
DAASUMP	1.72	2.14
ETH102E	4.98	2.31
C370FSH	1.88	2.04
C37036	3.57	1.97
C37072	3.89	1.69
C370108	5.10	2.02
SAABEOT	4.53	6.79
SHELLFSH	0.54	0.77
SHELLSUMP	3.48	4.27
ETHNO6	18.13	17.14

The differences between the integral regions X and Y obtained from the matching fresh and used oil dialysate infrared spectra are given in Table 4.d. This was not possible for samples ETH102E and ETHNO6 as the corresponding fresh oils were not obtained. However, the assumption was made that the corresponding fresh diesel oil was similar in chemical composition to ETHFSH and that the corresponding gasoline oil was similar in composition to C370FSH.

Table 4.d

Used - Fresh	Region X	Region Y
Q8TRZ - Q8LSREF	1.05	-0.02
Q8SUMP - Q8LSREF	0.01	-0.06
ETHTRZ - ETHFSH	0.38	0.34
ETH102E - ETHFSH	2.74	0.48
ETHSUMP - ETHFSH	-0.17	-0.02
DAASUMP - DAAFSH	-0.63	0.38
C37036 - C370FSH	1.69	-0.43
C37072 - C370FSH	2.01	-0.35
C370108 - C370FSH	3.22	-0.02
SAABEOT - C370FSH	2.65	4.75
ETHNO6 - C370FSH	16.25	15.10
SHELLSUMP - SHELLFSH	2.94	3.5

The fresh oils alone therefore have zero values for regions X and Y.

Interestingly the only oils which show a significant increase in region Y are those from gasoline engines which contain low volatile components, as indicated by the thermogravimetric work. A sample of leaded four star fuel was therefore examined by infrared spectroscopy, the spectrum is shown in Figure 4.n.

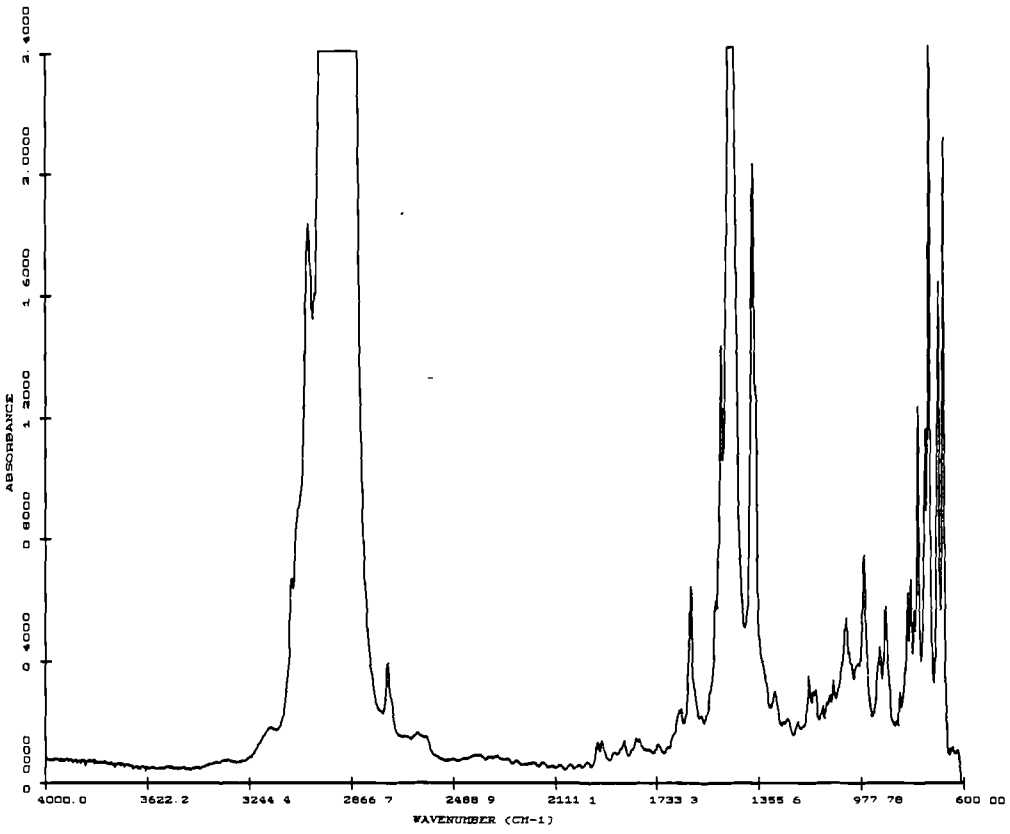


Figure 4.n

The IR spectrum shows absorbance around 1600cm^{-1} assigned to aromatic rings, which partially explains the increase in absorbance in this region for the fuel diluted gasoline oil samples. There is also the fuel characteristic absorbance in the lower wavenumber region of the spectrum. It is therefore impossible to differentiate between nitration species due to oxidation and fuel contamination, on the basis of infrared spectroscopy alone.

Coates and Setti [26] reported that fuel dilution can result in the apparent loss of ZDDP as determined from an IR difference spectra. They also suggested that degradation products mask the effect of fuel contamination in the carbonyl region of the IR spectrum.

Analysis of the dialysates yields valuable information regarding the extent of oxidation present within a used oil. The major advantages of the method include;

1. Insoluble matter remains in the residue fraction.

2. Additives which absorb in the carbonyl region of the spectrum are retained almost exclusively in the residue fraction.

3. The technique is simple and effective.

The disadvantages of the method are;

1. Any oxidation products with molecular weights above about 2000 will also be retained in the residue.

2. The dialysis procedure is time consuming.

4.3.3 Liquid Phase Chromatography

A 10g sample of the fresh Ethyl diesel oil, ETHFSH, dissolved in 30 ml of pentane was loaded onto 25g of silica gel and eluted with 90ml of pentane and 150ml of dry methanol, using the method described earlier. The infrared spectra of the samples are given in Figure 4.o.

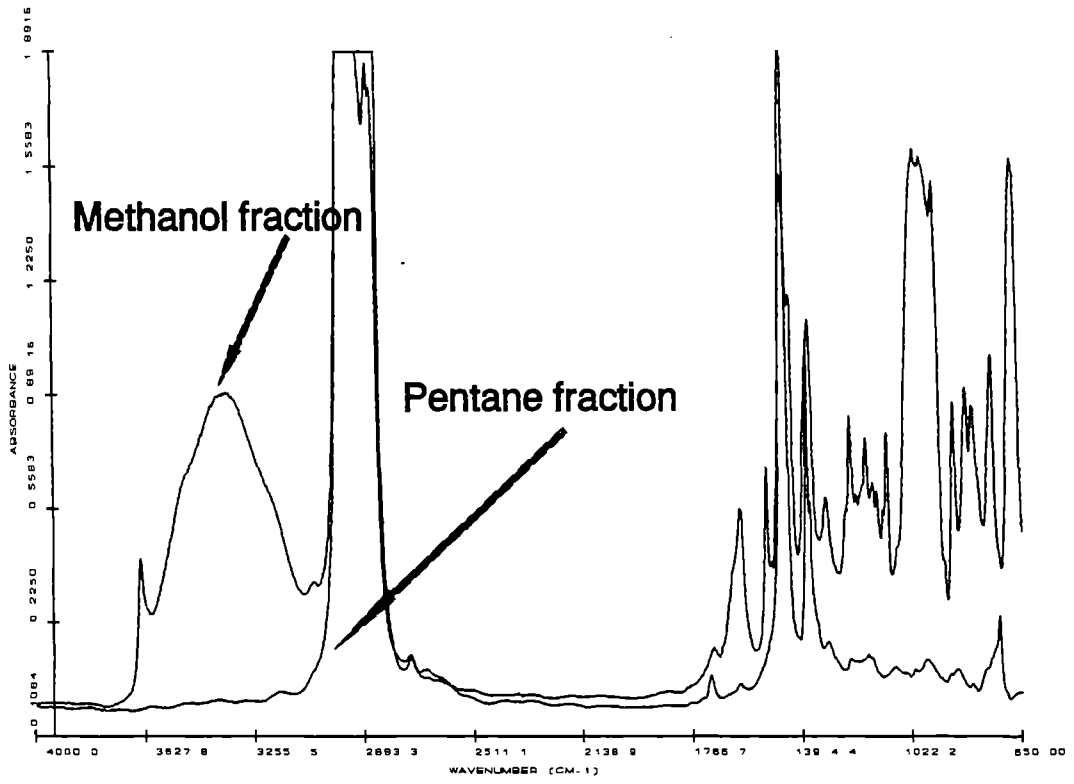


Figure 4.o

The methanol was very difficult to remove from the polar fraction, the broad band from 3000cm^{-1}to 3600cm^{-1} indicating methanol, water contamination. The infrared spectrum of the non-polar fraction showed an absorption at 1700cm^{-1} which was unexpected. Repetition of the experiment showed the same results. The same experiment was conducted but without the oil sample ie a blank run. The pentane collected was reduced to a small sample and analysed by infrared spectroscopy, the spectra shown in Figure 4.p.

No carbonyl peak was observed from the blank run spectrum. The pentane did not therefore contain significant impurities. A more detailed experiment was then carried out where 50ml samples were collected as the column was eluted with solvent.

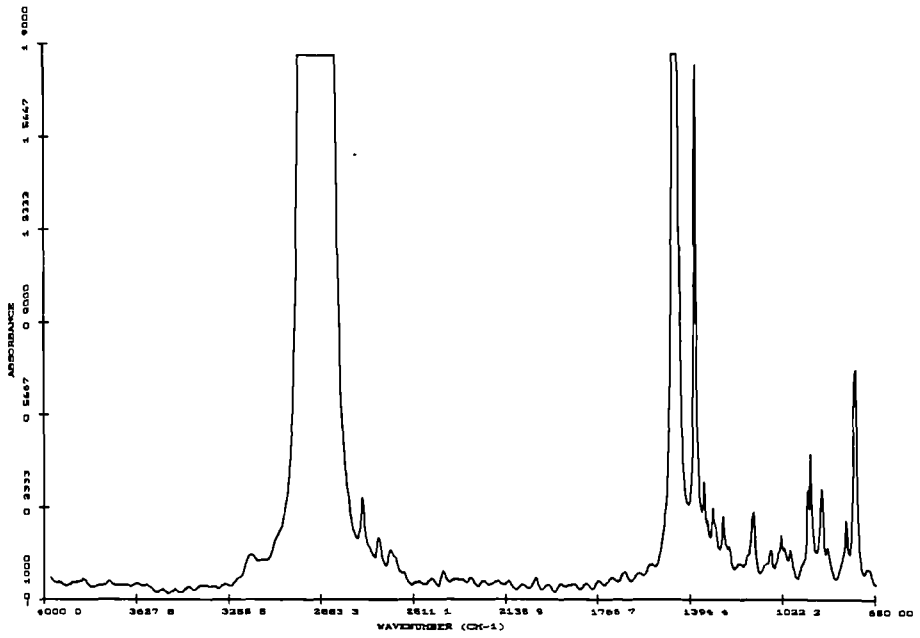


Figure 4.p

A 10g sample (ETHFSH) was dissolved in 25ml of pentane and loaded onto 40g of silica gel, using the apparatus shown previously. 50ml additions of pentane were applied in succession to the column, collecting 50ml fractions from the conical flask until a total of 300 ml had been added (6 samples). The column was dried using the vacuum pump and then eluted with 300ml of diethyl ether, collecting 100ml fractions (3 samples). Diethyl ether was used instead of methanol as it is a very volatile solvent and therefore simple to remove. The bulk of the solvent from each sample was removed using a rotary evaporator and the last traces by gentle heating on an oil bath kept below 100°C. The sample weights were recorded for each sample followed by infrared analysis. The sample weights are given in Table 4.e.

Table 4.e

Sample	Mass/g
1	1.12
2	7.32
3	1.23
4	0.20
5	0.10
6	0.07
7	0.24
8	0.18
9	0.03

The infrared spectra of the nine samples are shown in Figures 4.q-4.t.

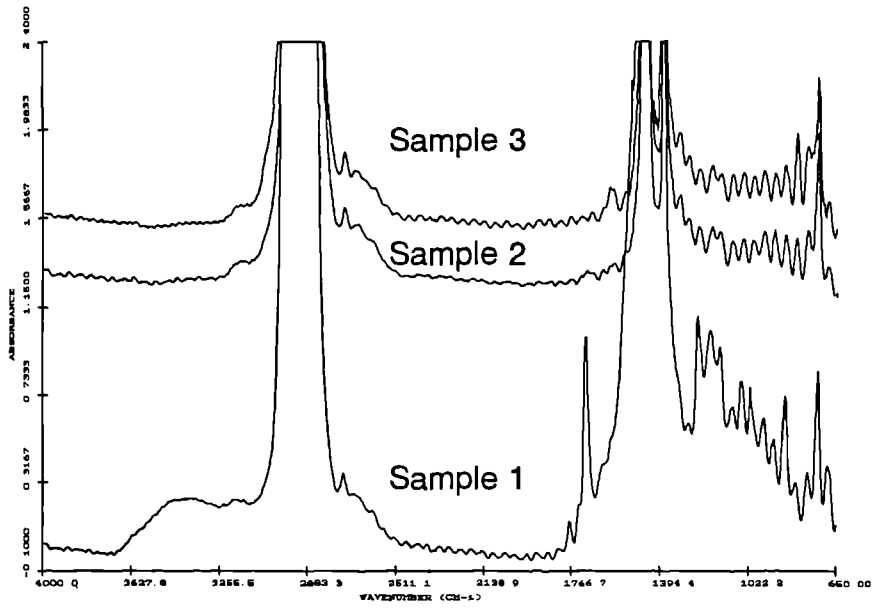


Figure 4.q Samples 1-3

The spectra of sample 1 shows that species were present other than pure hydrocarbons, noticeably the PIB succinimide.

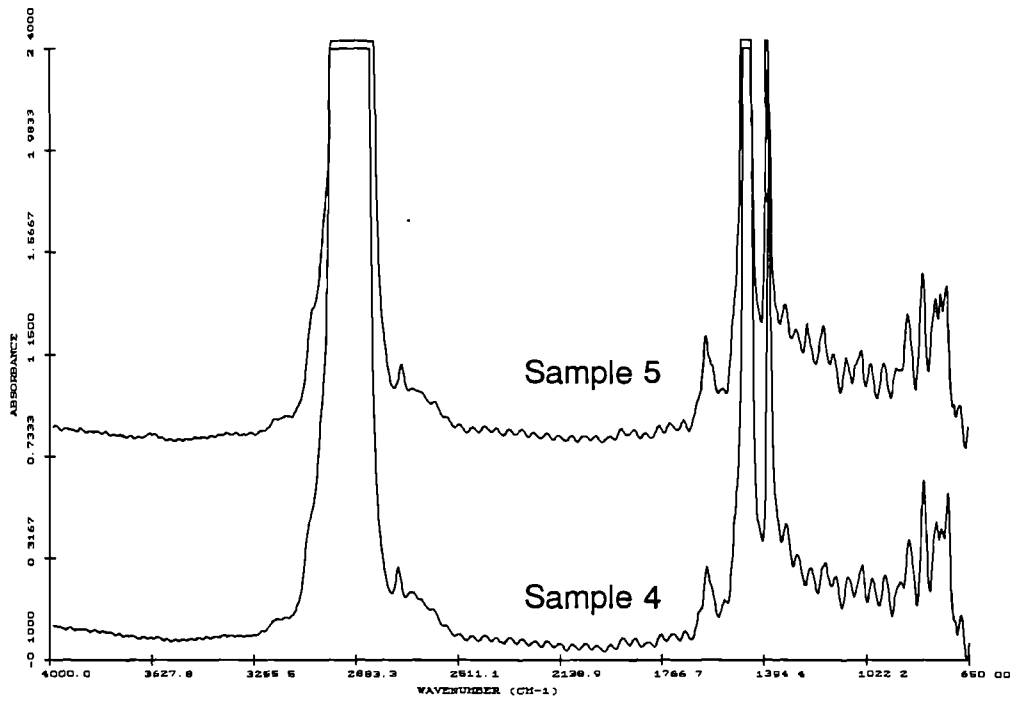


Figure 4.r Samples 4 and 5

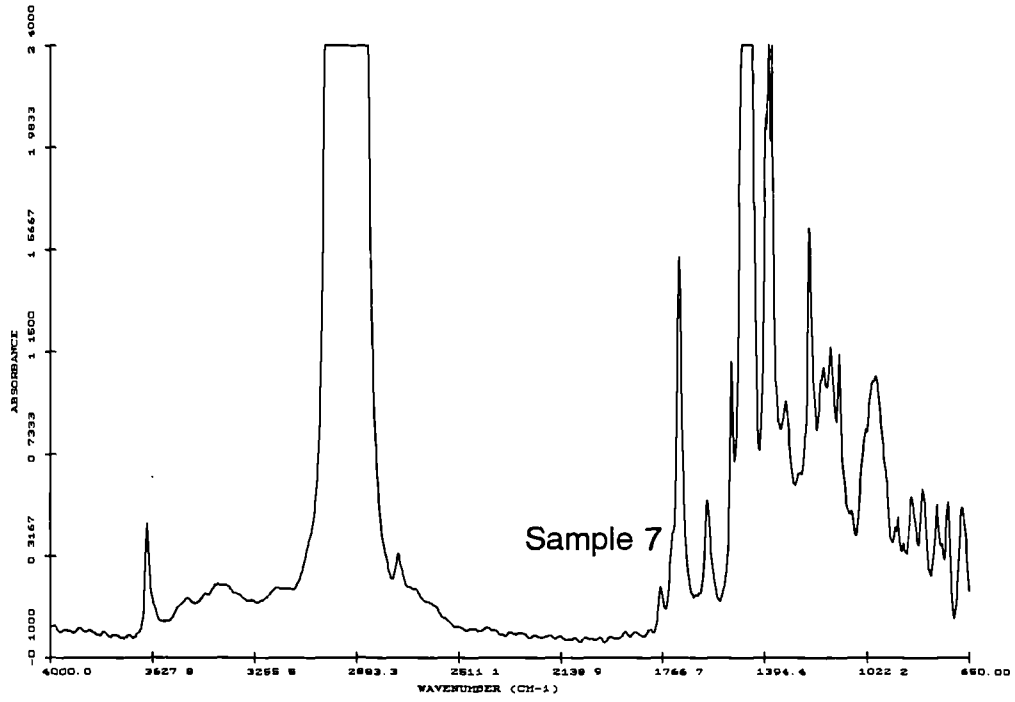


Figure 4.s Sample 7

The spectra of samples 4 and 5 show absorption at 1600cm^{-1}, due to aromatic species. Sample 6 was too small to analyse but was probably similar in composition to sample 5. Sample 7 was the first sample to be eluted with diethyl ether. The spectra of sample 7 shows the phenolic antioxidant at 3648cm^{-1}, the PIB succinimide at 1771cm^{-1} and 1704cm^{-1}, aromatic ring at 1600cm^{-1}, ZDDP at 1000cm^{-1}, and peaks due to hydrocarbon.

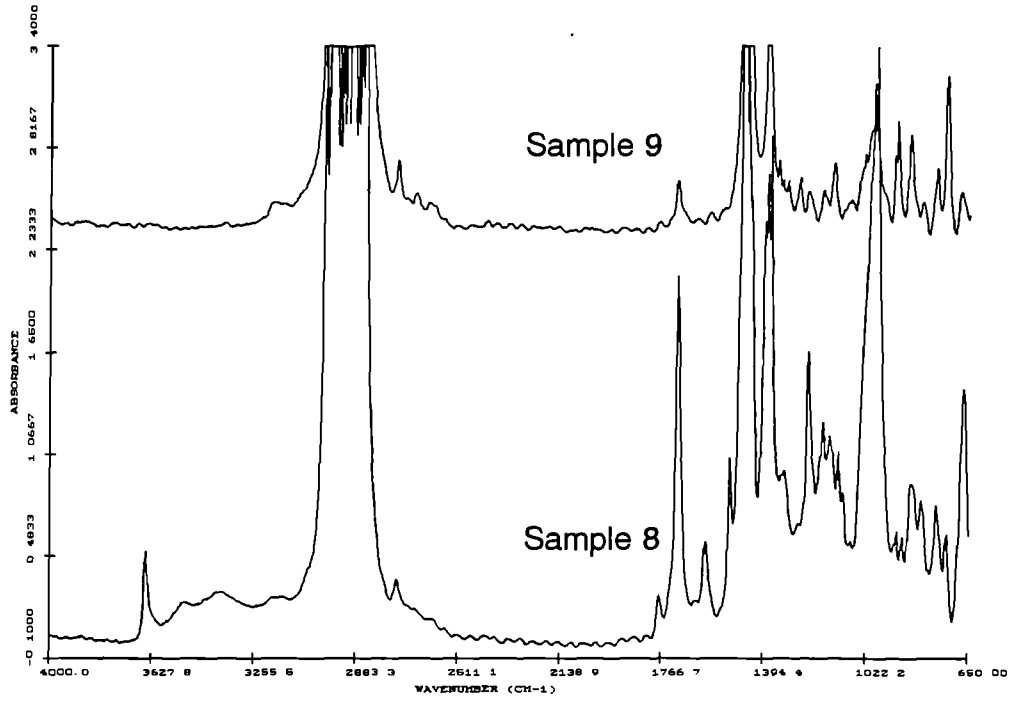


Figure 4.t Samples 8 and 9

The spectra shown in Figure 4.t show that sample 8 was very similar to sample 7, except that the absorption due to the ZDDP was more intense. Sample 9 did not contain significant amounts of additive either because all the additives had been eluted or that they were strongly absorbed onto the silica gel.

To isolate and quantify the oxidative products was more complicated than initially anticipated. As the dialysis method was so successful the liquid chromatographic

method was not pursued further. It could prove to be a valuable method for qualifying, and possibly quantifying certain additives in oil formulated products.

4.4 Conclusion

The infrared analysis of fresh and used lubricating oils can be simplified by separating the samples prior to analysis. Dialysis was found to be a significantly more useful technique than liquid phase chromatography.

The interpretation of the neat infrared spectra was complicated by;

1. Contamination by soot and other insoluble matter.
2. The presence of additives which absorb in the same region of the spectrum as degradation products, particularly carbonyl species.
3. Contamination by fuel.
4. The possibility of additive concentration due to loss of base oil.

The dialysis procedure was a good method for examining the oxidative degradation products because;

1. The soot and insoluble matter remained in the residue.
2. Oxidation products diffused through the membrane wall into the dialysate.
3. High molecular weight additives, including those containing carbonyl functional groups, remained in the residue.
4. The repeatability of the method was good.

The separation of the base oil from the additives using liquid chromatography was not very successful as it was difficult to recover the additives, and possibly oxidation products, from the silica gel. The method could be used however for the separation and analysis of the base oil alone.

CHAPTER 5 Four Ball Tester

5.1 Background

In 1933 McKee et al [38] reported the work undertaken by the US Bureau of Standards, in collaboration with the SAE Lubricants Research Subcommittee, on the problem of extreme pressure lubricants. A study was made of the performance of four machines determining the load necessary to produce seizure for a range of extreme pressure lubricants. Further studies included the comparison of results obtained for one oil at a range of temperatures. The results concluded that:

1) The four lubricant-testing machines, when operated as recommended by the manufacturers, did not rate the lubricants in the same order. No suitable operating conditions were found for each machine such that they were rated the same.

2) The load carrying properties of extreme pressure lubricants tend to decrease as the temperature increases.

3) The load carrying properties of extreme pressure lubricants tend to decrease as the rubbing speed increases.

4) The effects of speed and temperature differ with the particular lubricant and machine involved to such an extent that even the order of rating may be changed.

5) The ratio of the applied load to the actual pressure changes rapidly on running with each of the four machines, which threw doubt on the comparability of each machine.

Around the same time Boerlage [39] described a new machine for testing extreme pressure lubricants, the "Four Ball Testing Apparatus". It was designed with the objective of providing an instrument which gave useful results both rapidly and cheaply. The moving surfaces of the apparatus consisted of chrome plated steel balls, such as those used in ordinary ball bearings. The balls were arranged in the form of a pyramid, three of them clamped tightly together with a conical ring in a cup of oil under test. The fourth ball rested on the other three and was held in a cup shaped shaft. A force was applied on the balls and the top ball then rotated under load by a pulley, driven by an electric motor. The friction of the balls tended to rotate the cup, which was on a table, itself supported on ball bearings. The torque on the table was measured by a spring dynamometer. The apparatus was run under many different conditions, the pressures, speeds, temperatures, and length of time of the test all varied. The quickest and most easily obtained results were determined by the highest pressure applied under constant speed that the oil would withstand in one minute without permitting seizure. The author pointed out that at a too high applied force the balls welded together so firmly that they were of no further use, except as paper weights.

Blok wrote several papers following the introduction of the Four Ball Tester, designed by his Director Boerlage. An illustration of the apparatus as given in a paper in 1939 [40], describing the seizure-delay method for determining the seizure protection of extreme pressure lubricants, looks almost identical to that of the present day Four-Ball Apparatus. Because of its geometry, the four ball contact cannot utilise a pure hydrodynamic film for load support. This was proven theoretically by Howlett in 1946 [41]. More recently, in 1985, it was shown that the thin film, boundary and scuffing regimes of lubricants which occur in a Four-Ball machine depend on the operating conditions such as speed, load and temperature [42]. The thin film zone is one of low friction and negligible wear which exists at small loads. The load is carried partly by an elastohydrodynamic film and partly by contact asperities. When conditions are more severe the thin film fails resulting in scuffing during which friction and wear suddenly increase.

This failure is referred to as 'seizure' in the Four Ball test. If the conditions are relatively mild the system recovers to a zone of low and steady friction resulting from a combination of oxidation of the contact surfaces, increase in contact area due to metal to metal contact and therefore reduction of contact pressure. In this zone the load is mainly carried by a boundary lubricant film. If the conditions are made more severe boundary lubrication fails leading to welding of the balls. In 1990 Inoue and Yamanaka [43] reported the use of the four ball test to determine the anti-wear properties of used oils obtained from a Toyota 1500cc engine bench test. The experimental conditions used were: operating temperature = 80°C, load = 30kg, revolution speed = 1200rpm, duration time = 30 minutes. The anti-wear performance was expressed as wear scar in mm. Another recent paper [44] published in 1991 describes the extreme pressure activity of some 2-phenyl-3-phenylimino-5-arylimino-1,2,4-thiadiazolidines, as shown by the four ball test. The following experimental conditions were used: revolution speed = 1475 rev/min, duration time = 60 seconds, load range = 56-500 kg. The wear scars were plotted against load for each sample as a means of comparison.

The four ball test is now one of the best known lubricant test machines, the results from which have been used in the development of hundreds of successful lubricants. It has been the basis of test methods standardised by the British Institute of Petroleum (IP method 239), the American Society for Testing and Materials (ASTM method D-2596) and other standard organisations. As the contact conditions in the Four Ball machine rarely mimic those in service it has been used more for quality control, fundamental research and development work. The detailed description of the experimental procedures, apparatus and analysis of results are given by IP 239. Figure 5.a. shows the Four Ball Test apparatus.

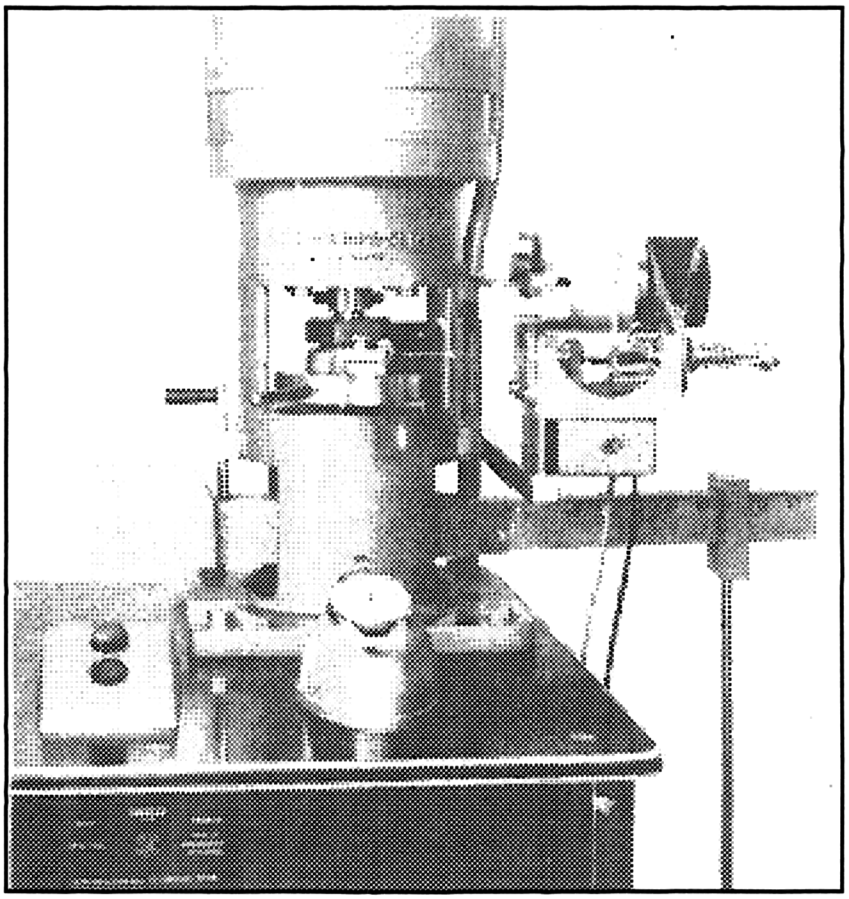


Figure 5.a

A Four Ball Testing Machine was available for use at De Montfort University. The experimental procedure described below was based on the determination of "Mean Hertz Load", as described by the IP 239 test method. This however required a minimum of 20 tests per oil which was not only time consuming but also required approximately 200ml of oil. Due to the small samples obtained from the top ring zone it was necessary to modify the Four Ball apparatus.

5.2 Modification of Four Ball Apparatus

The amount of lubricant required per experiment is approximately 8ml. This was reduced to 1.5ml by essentially removing the "dead" volume around the four balls by redesigning the sample cup holder and clamping ring. The photographs in Figures 5.b and 5.c compare both the old and new sample cup and clamping ring.

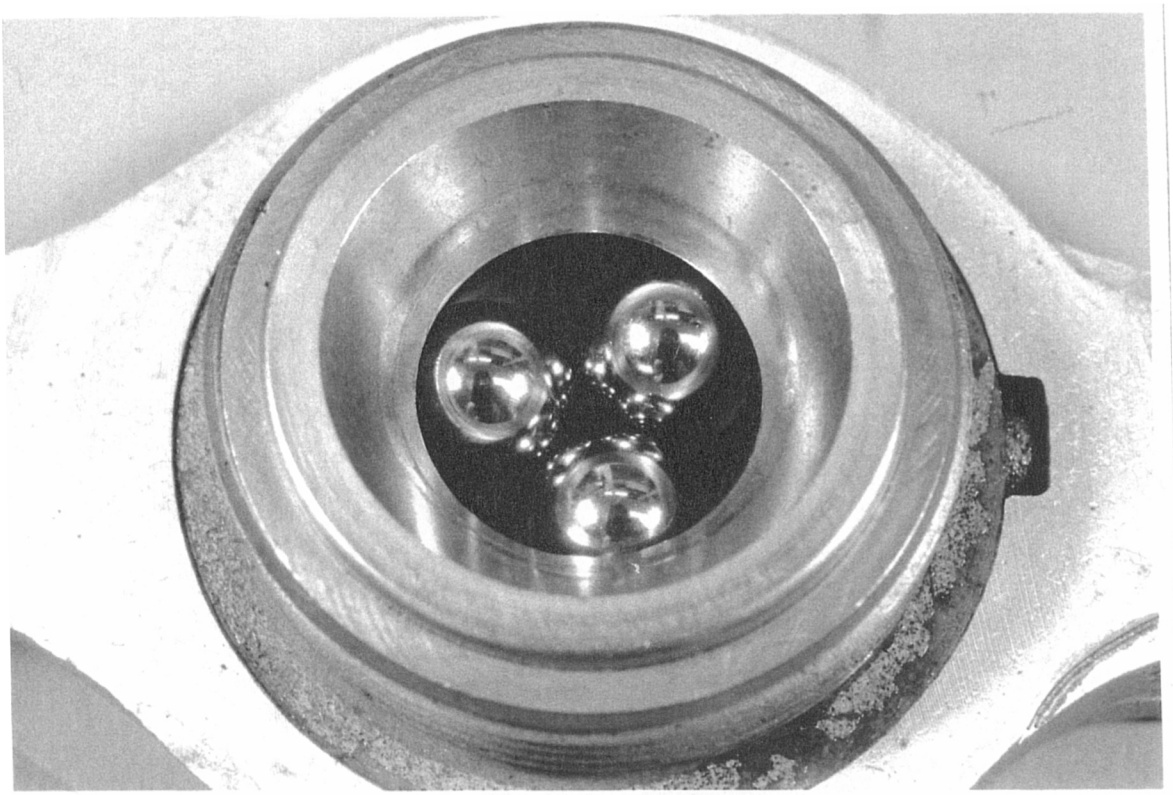


Figure 5.b Original Cup and Clamping Ring

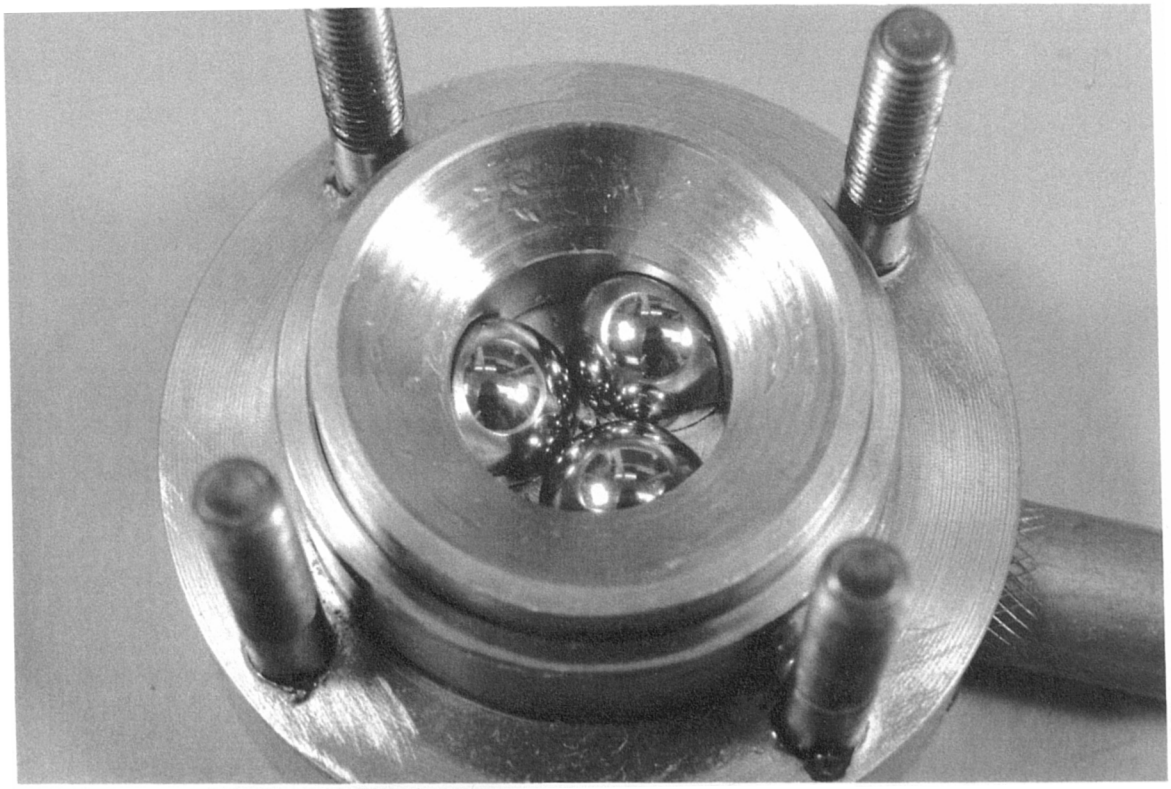


Figure 5.c Modified Cup and Clamping Ring

5.3 Experimental Procedure

Three balls were placed into the cup holder followed by the minimum amount of lubricant and clamped securely by means of the clamping ring and locking nut. The fourth ball was inserted into the chuck and then mounted into the chuck holder. The cup assembly was supported above the load lever by a disc which rested on a thrust bearing, allowing horizontal displacement and automatic alignment of the three lower balls against the upper ball. Weights were then hung from the horizontal arm and the load applied to the balls. The arm of the cup was attached to the spring of the friction recording device. Different springs were used according to the load applied, the greater the load the larger the spring. The motor was run for 10 seconds causing the upper ball to rotate against the three lower balls. The load was then released, ball assembly removed, upper ball discarded and measurements were taken of the scars produced on the lower three balls. The apparatus was then cleaned thoroughly before repeating the whole procedure except with a different load, until the maximum load had been applied resulting in welding of the balls.

5.4 Description of Samples

Sample name	Description
C370FSH	Fresh mineral based multigrade gasoline lubricant
C370108	Oil taken from a Petter W1 at Castrol Research Centre after a period of 108 hours, where the fresh oil was C370FSH
SAABEOT	The C370FSH oil was also run in a Saab engine test. This was the oil sample collected at the end of the test.
C370TRZ	A top ring zone sample taken from a Petter AA1 diesel engine, where the fresh oil was C370FSH.
X311FSH	Fresh mineral based monograde oil.
X311TRZ	A top ring zone sample taken from a Petter W1 gasoline

engine, the fresh oil was X311FSH.

XF29FSH	A fresh fully synthetic multigrade gasoline oil.
150SN	A fresh 150 solvent neutral base oil.
500SN	A fresh 500 solvent neutral base oil.

5.5 Results

At the end of each experiment the average wear scar diameter (mm) was calculated and plotted against the load applied (kg). A typical plot is shown below.

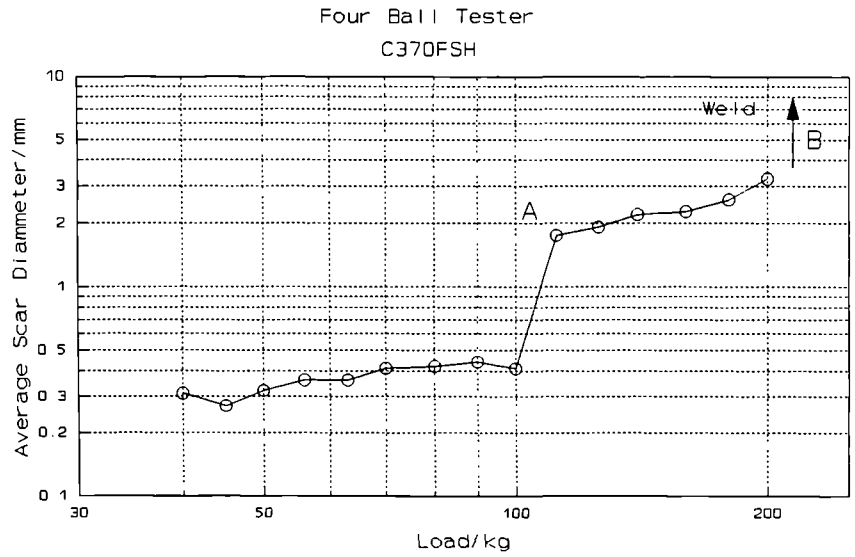


Figure 5.d

The load at which initial seizure occurred, point A, corresponds to the failure of the thin film present. The welding load, point B corresponds to failure of the boundary lubrication. Typical wear scars are shown in Figures 5.e and 5.f, corresponding to the region before and after point A.

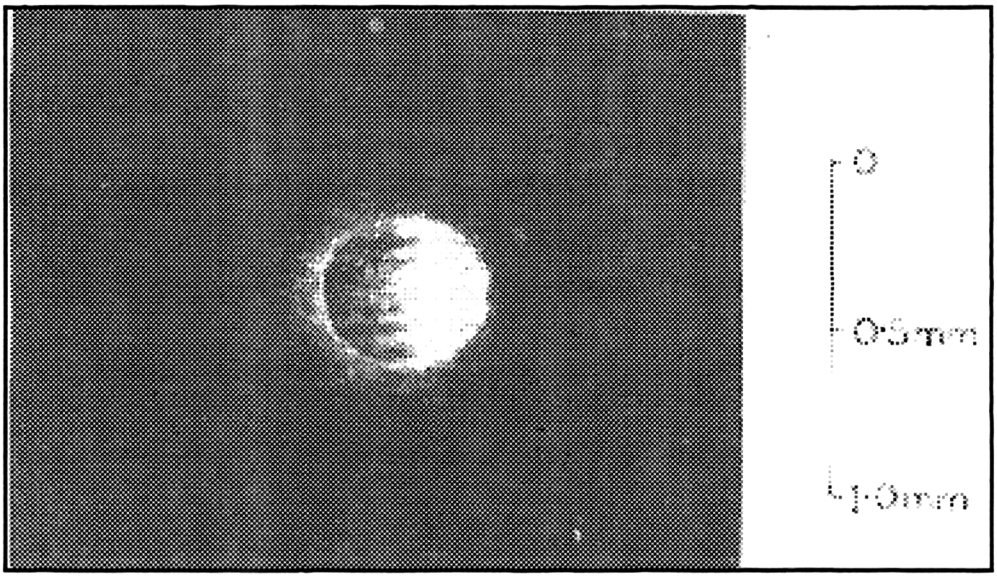


Figure 5.e Typical Low Wear Scar Before Seizure

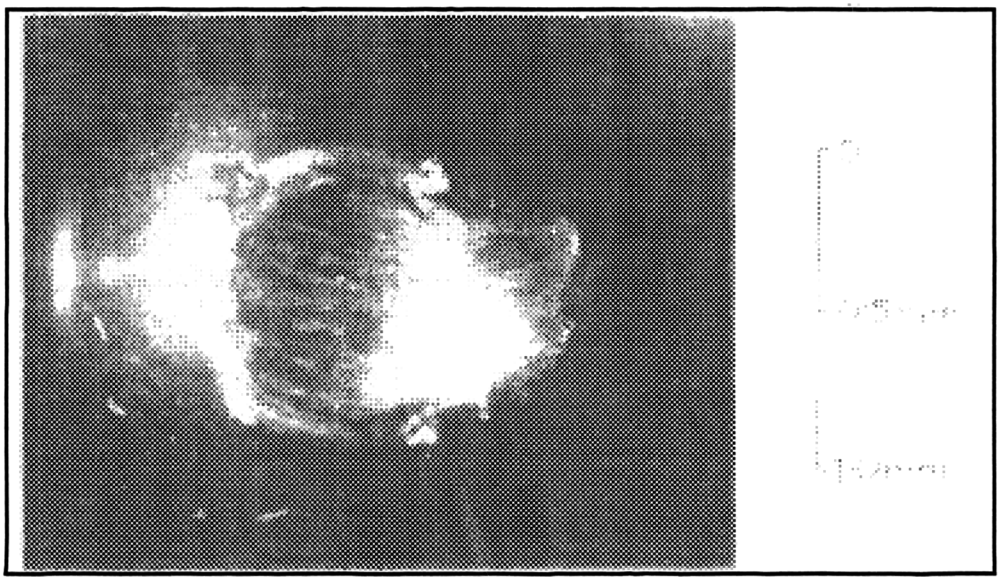


Figure 5.f Typical High Wear Scar After Seizure

The initial seizure load and weld load were determined for each sample, as shown from the scar versus load plot. The results obtained for the oils described in 5.4 are given in Table 5.a.

Table 5.a

Sample Name	Original/modified cup and clamp	Initial Seizure Load/kg	Weld Load/kg
C370FSH	Original	112	224
C370FSH	Modified	126	224
C370FSH	Original	112	224
C370FSH	Modified	126	250
C370FSH	Original	126	225
C370108	Original	112	251
C370108	Modified	112	-----
SAABEOT	Modified	63	225
SAABEOT	Original	70	225
C370TRZ	Modified	112	250
X311FSH	Original	112	200
X311TRZ	Modified	90	200
XF29FSH	Original	158	224
XF29FSH	Modified	160	225
150SNFSH	Original	56	158
500SNFSH	Original	79	158

5.6 Discussion

A plot of the average wear scar diameter versus load applied for each of the experiments carried out on C370FSH, using both the original and modified apparatus is shown in Figure 5.g.

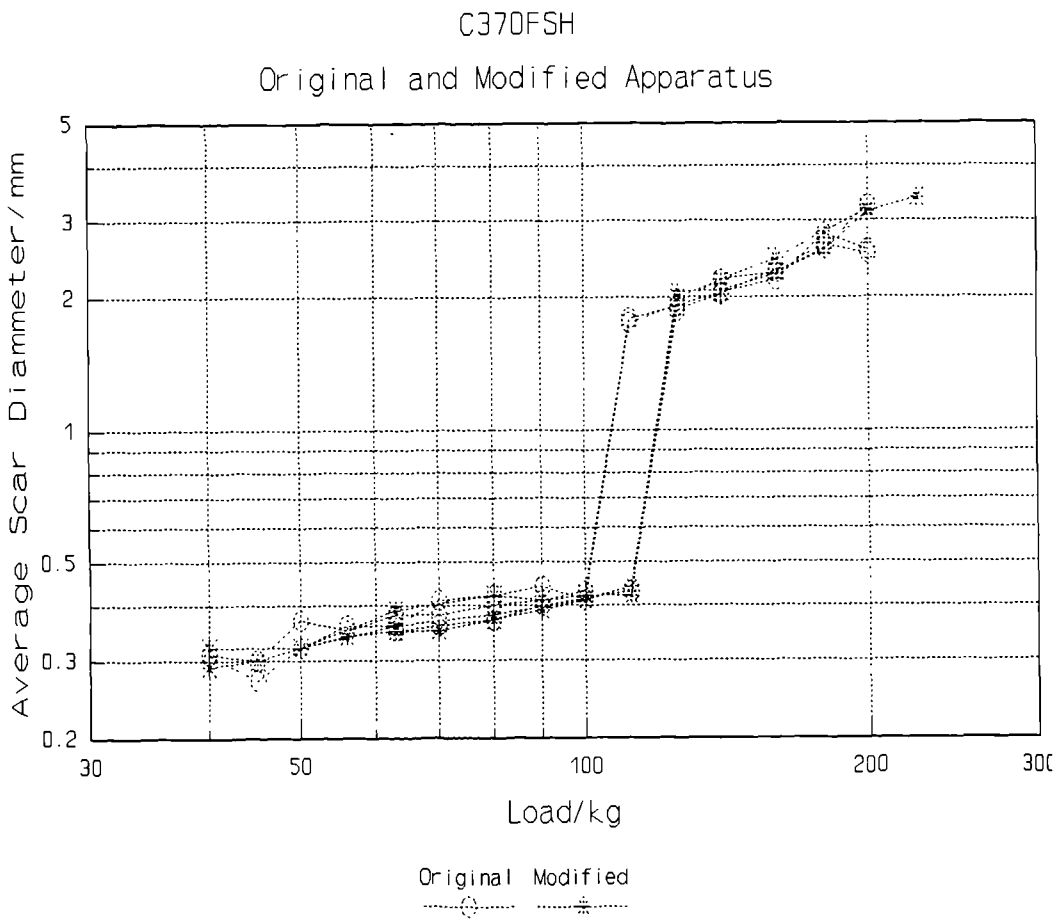


Figure 5.g

Similar results are obtained using either the original or modified apparatus. The initial seizure and weld loads are only accurate to within one load stage, which is consistent with the IP method.

Taking the average values of both initial seizure and weld load where applicable a bar chart was constructed showing the results obtained from the different oil samples, Figure 5.h.

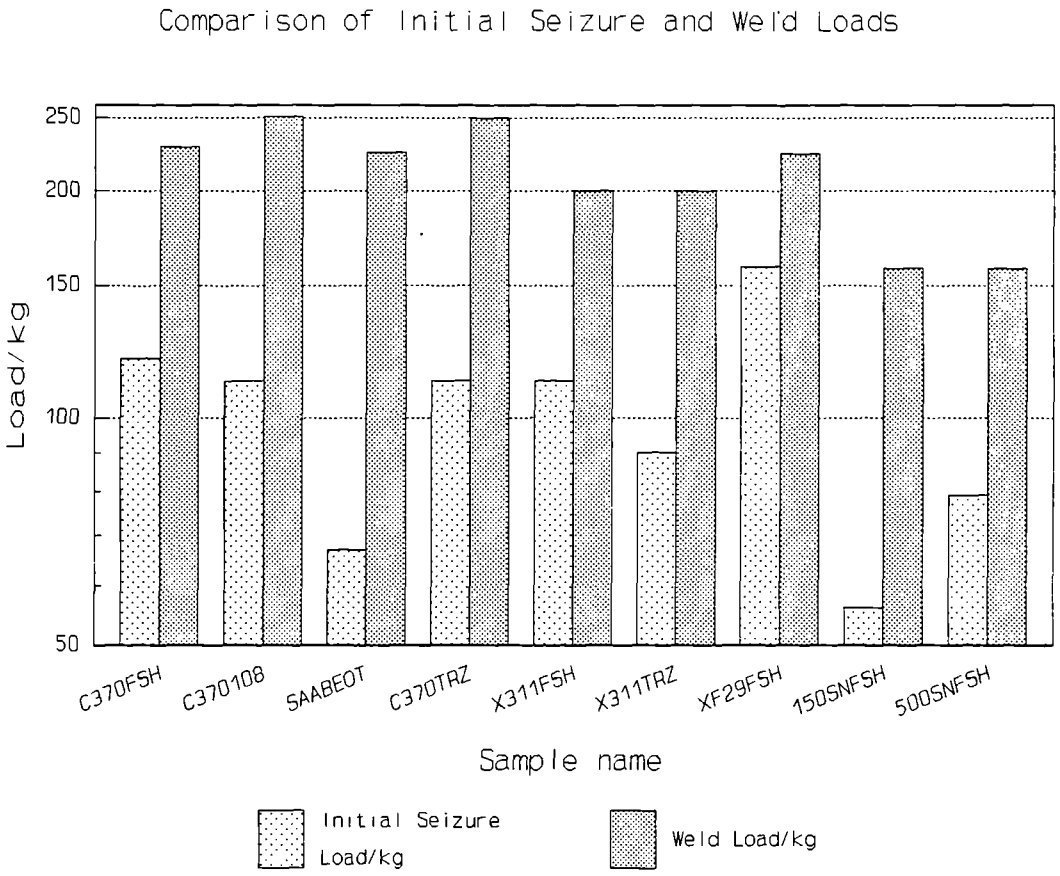


Figure 5.h

From the bar chart the following observations were made:

1) The thin film lubrication present with XF29FSH was capable of carrying a significantly greater load than any of the other samples.

2) Both the base oils were less able to support boundary lubrication, as shown by the low weld loads.

3) The higher viscosity base oil, 500SNFSH, formed a more effective thin film layer than the low viscosity base oil, as shown by the higher initial seizure load.

4) The Saab end of test oil, SAABEOT, had poor low load properties, as indicated by the low initial seizure load.

5) Comparison of the fresh and top ring zone monograde samples, X311FSH and X311TRZ respectively, showed that top ring zone sample had poorer low load properties.

The viscosity of the lubricant is obviously important in the region of thin film lubrication. This is reflected by the initial seizure loads of the samples. The differences observed between the initial seizure loads of the oil samples were thought to be primarily due to their viscosities. Degradation of anti-wear additives could also be responsible for a decrease in initial seizure load results obtained. The change in viscosity of a used oil can be attributed to one or more of the following;

1. Fuel dilution - decrease in viscosity
2. Soot/other insolubles - increase in viscosity
3. Oxidation of oil - increase in viscosity
4. Evaporation of volatiles - increase in viscosity

The degraded end-of-engine-test gasoline oil, named SAABEOT, had poor low load properties. From the thermogravimetric work described in Chapter 2 this oil contained a significant amount of high volatile components, assumed to be fuel contamination. Fuel contamination would result in a decrease in the overall viscosity and dilution of the additives present within the formulated oil. Coates and Setti [26] have shown that a decrease in ZDDP can be observed as a result of a volumetric displacement of lubricant components by added fuel. The poor thin film properties of this oil were therefore probably due to a combination of viscosity decrease and dilution of additives. The top ring zone sample, X311TRZ, taken from a Petter W1 gasoline engine also exhibited poor thin film properties. Previous work has shown that top ring zone samples from this engine are

contaminated with fuel. The poor results were similar to those obtained by SAABEOT, only to a lesser degree, for the same reasons. The fully synthetic oil, XF29FSH, was capable of carrying a significantly greater load than any of the other oils tested, in the thin film regime. As the formulation of this product was not known it is difficult to predict whether the enhanced low load properties were due to the synthetic base oil or advanced additives.

In the boundary regime additives present within the oil samples can form important films between the metal surfaces preventing welding from occurring. No significant differences were observed between the samples except the base oils which obviously do not contain additives.

5.7 Conclusion

The modified apparatus successfully reduced the volume of sample required from 8ml to 1.5 ml per run. In order to determine the initial seizure load and weld load a minimum of 9 ml was required. This required the majority if not all of a top ring zone sample collected over 9 hours. If other analyses are to be carried out the total amount of sample needed would require longer engine runs, which then reduces the benefit of top ring zone sampling. Alternatively a different Four Ball Test method could be developed which requires one experiment per oil, and therefore would only require a 1.5 ml sample. Such a method was described by Inoue and Yamanaka [43], where the anti-wear performance was expressed as wear scar in mm, at a very low load.

The results of used oils, obtained from any Four Ball Test method, cannot be directly compared without considering the viscosity changes produced by oxidation, fuel and/or soot contamination and evaporative losses. As complete specifications were not obtained for the fresh oils, and insufficient sample volume was collected from top ring zone sampling, viscosity measurements were not obtained.

CHAPTER 6 Interpretation of Results

6.1 Introduction

To evaluate the degree of degradation of an oil all the results from the various analyses must be examined together. Comparing the fresh and used oils based on one variable alone, for example Base Number, can lead to misleading conclusions. For example, loss of base oil due to evaporation would result in an increase in Base Number, due to concentration of the additives. A used oil could therefore have a Base Number equivalent to its corresponding fresh oil due to a combination of evaporative losses and decrease in Base Number. Similarly by subtracting the infrared spectrum of a fresh oil from that of a used oil could result in the apparent observation of carbonyl oxidation, due to the concentration of the polyisobutenylsuccinimide dispersant in the used oil. Evaporation of base oil is particularly significant with top ring zone samples. It is relatively simple to plot one parameter against another, for example Base Number versus Acid Number, resulting in numerous plots which must then be brought together. A method which is capable of comparing all parameters simultaneously would therefore be infinitely desirable. The results obtained from both fresh and used lubricating oils were therefore examined using a method known as "Principal Component Analysis" (PCA).

6.2 Summary of Results

The results discussed in Chapters 2-4 are summarised in Table 6.a, where

Relative volatility = Average relative volatility - Chapter 2
Base Number = Average Base Number / mg KOH/g oil - Chapter 3
Acid Number = Average Acid Number / mg KOH/g oil - Chapter 3
IRX = Integral Region X from dialysate spectra - Chapter 4
IRY = Integral Region Y from dialysate spectra - Chapter 4

Table 6.a

Sample	Relative Volatility	Base Number	Acid Number	IRX	IRY
Q8LSREF	1.435	9.40	0.35	0	0
Q8TRZ	0.992	9.90	0.15	1.05	-0.01
Q8SUMP	1.363	9.10	0.60	0.02	-0.06
ETHFSH	1.057	9.40	-0.95	0	0
ETHTRZ	0.798	8.55	3.35	0.38	0.33
ETHSUMP	1.065	8.75	-2.10	-0.17	-0.02
DAAFSH	1.210	9.20	-0.35	0	0
DAASUMP	1.008	7.10	0.15	-0.63	0.38
ETH102E	0.839	8.95	0.65	2.74	0.47
C370FSH	1.049	7.55	0.15	0	0
C37036	0.831	7.20	-0.05	1.68	-0.07
C37072	0.710	8.05	0.10	2.01	-0.34
C370108	0.613	8.00	0.50	3.22	-0.02
SAABEOT	1.000	2.45	1.30	2.64	4.75
SHELLFSH	1.073	6.50	0.50	0	0
SHELLSUMP	1.008	1.85	2.60	2.94	3.50
ETHNO6	1.476	1.90	2.35	16.24	15.10

6.3 Principal Component Analysis

The idea of Principal Component Analysis (PCA) was attributed to Pearson [45] in 1901. The current technique was not developed however until 1931, and was not introduced into chemistry until a further 30 years, since which time the application of the technique has become widespread. PCA is a technique used to reduce the number of variables in a dataset by finding linear combinations of these variables that explain most of the variability. Such combinations of the

variables are called Principal Components. The Principal Components can then be used to develop relationships between samples which might, for example, classify the data into groupings or highlight outliers. The results in this thesis have been examined using a software package called "Statgraphics", capable of calculating Principal Components from any given dataset. Using "Statgraphics" the Principal Components were calculated from the dataset set given in Table 6.a using all five variables (Base and Acid Number, relative volatility, regions X and Y from IR analysis). The results from the Principal Component Analysis are shown below.

Principal Component Analysis

Component Number	Percent of Variance	Cumulative Percentage
1	61.1	61.1
2	21.1	82.2
3	10.5	92.7
4	7.0	99.7
5	0.3	100.0

The PCA results show that the first Principal Component accounts for 61.1 percent of the total variability, while the next two components account for an additional 31 percent. The first two components account for 82 percent of the total variability. A plot of the component weights is shown Figure 6.a, which shows that the variables Relative volatility, IRX, IRY and Acid No positively weight Principal Component One whereas the variable Base No negatively weights Principal Component One. Similarly Base No, Relative volatility, IRX and IRY positively weight Principal Component Two whereas Acid No negatively weights Principal Component Two.

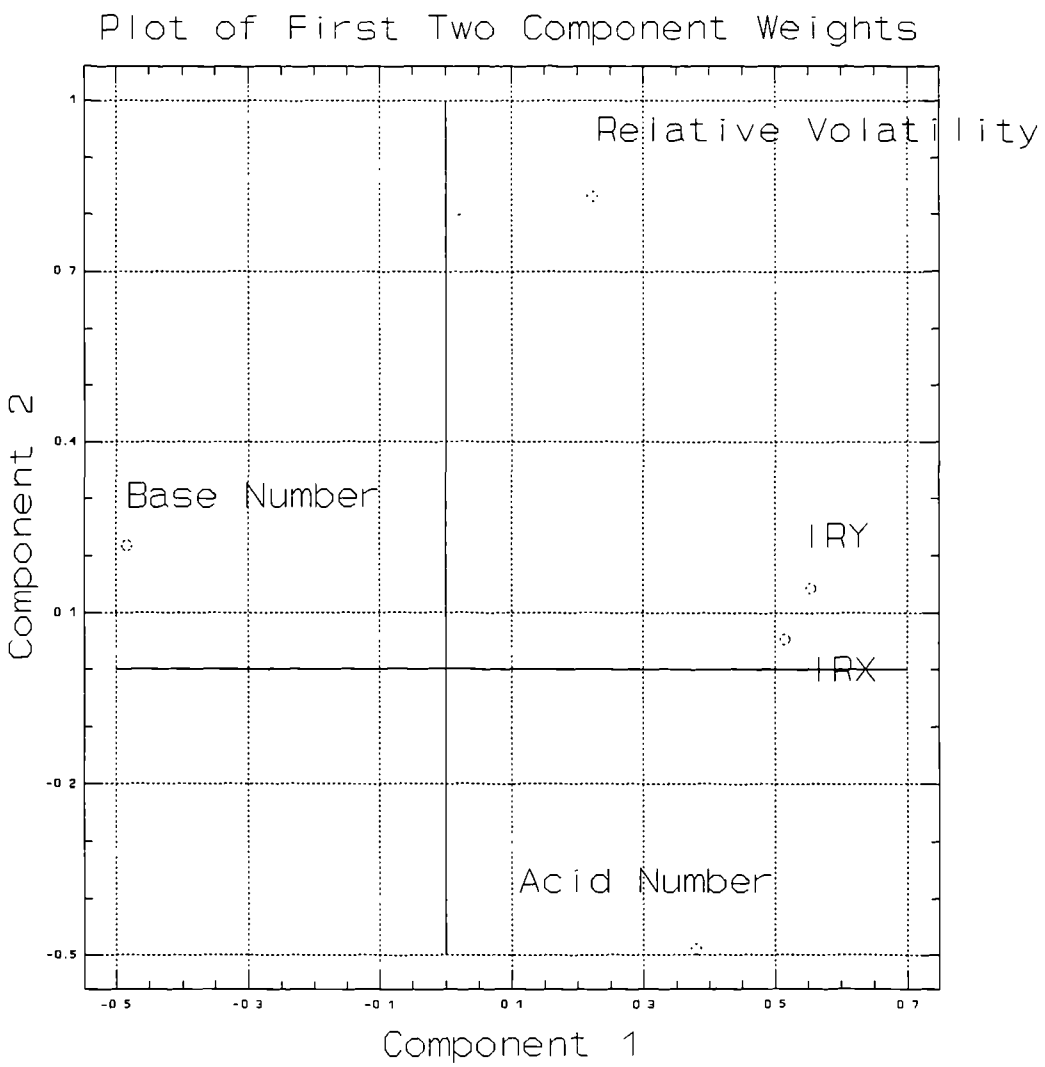


Figure 6.a

The first two Principal Component equations, PC1 and PC2, were determined, as given below.

Principal Component 1 (PC1) = 0.515 (IRX) + 0.554 (IRY) + 0.222 (Relative volatility) - 0.483 (Base No) + 0.380 (Acid No)

Principal Component 2 (PC2) = 0.054 (IRX) + 0.144 (IRY) + 0.830 (Relative volatility) + 0.219 (Base No) - 0.489 (Acid No)

A plot of the first two Principal Components is shown in Figure 6.b.

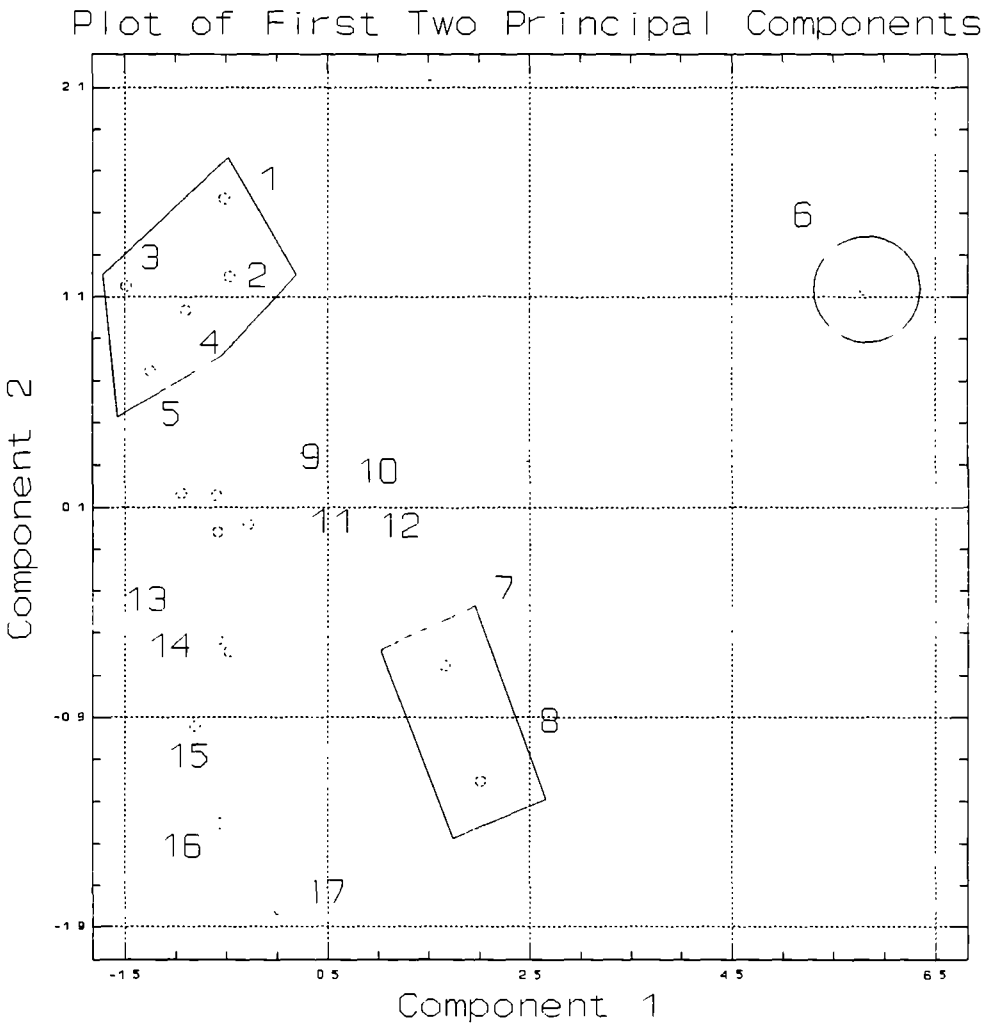


Figure 6.b

Each point labelled on the Principal Component scatterplot represents an oil sample, its position determined by PC1 and PC2, which are calculated from the equations given. Points close together on the scatterplot are therefore similar in character, based on the analyses carried out, and those which are separated on the scatterplot are therefore different in character. The oils labelled 1-17 on the scatterplot are listed below.

1 Q8LSREF	10 C370FSH
2 Q8SUMP	11 DAASUMP
3 ETHSUMP	12 SHELLFSH
4 DAAFSH	13 C37036
5 ETHFSH	14 ETH102E
6 ETHNO6	15 C37072
7 SAABEOT	16 C370108
8 SHELLSUMP	17 ETHTRZ
9 Q8TRZ	

Examination of the scatterplot shows that:

1) Principal Component One is <1 for the majority of samples, excluding those labelled 6,7 and 8 (highlighted). The latter represent the degraded gasoline oils as named above. These oils have high values for IRX and IRY, and have very low Base Numbers. ETHNO6 is obviously extensively degraded. Interestingly, PC2 for this oil is very high due to the high relative volatility. This is presumed to be due to the fuel contamination.

2) The points 10, 13, 15 and 16, show the variation in character in the oils taken from a Petter W1 at 36 hour intervals. As PC2 decreases so too does the relative volatility, which heavily weights PC2. PC1 does not change significantly for any of these samples.

3) The points labelled 1-5 represent the fresh diesel lubricating oils, including those oils taken from the Petter AA1 after a short duration (highlighted).

4) The points representing the two top ring zone samples (9 and 17) are not together on the scatterplot. PC2 is very low for ETHTRZ due to its high Acid Number.

The biplot for the first two components is shown in Figure 6.c.

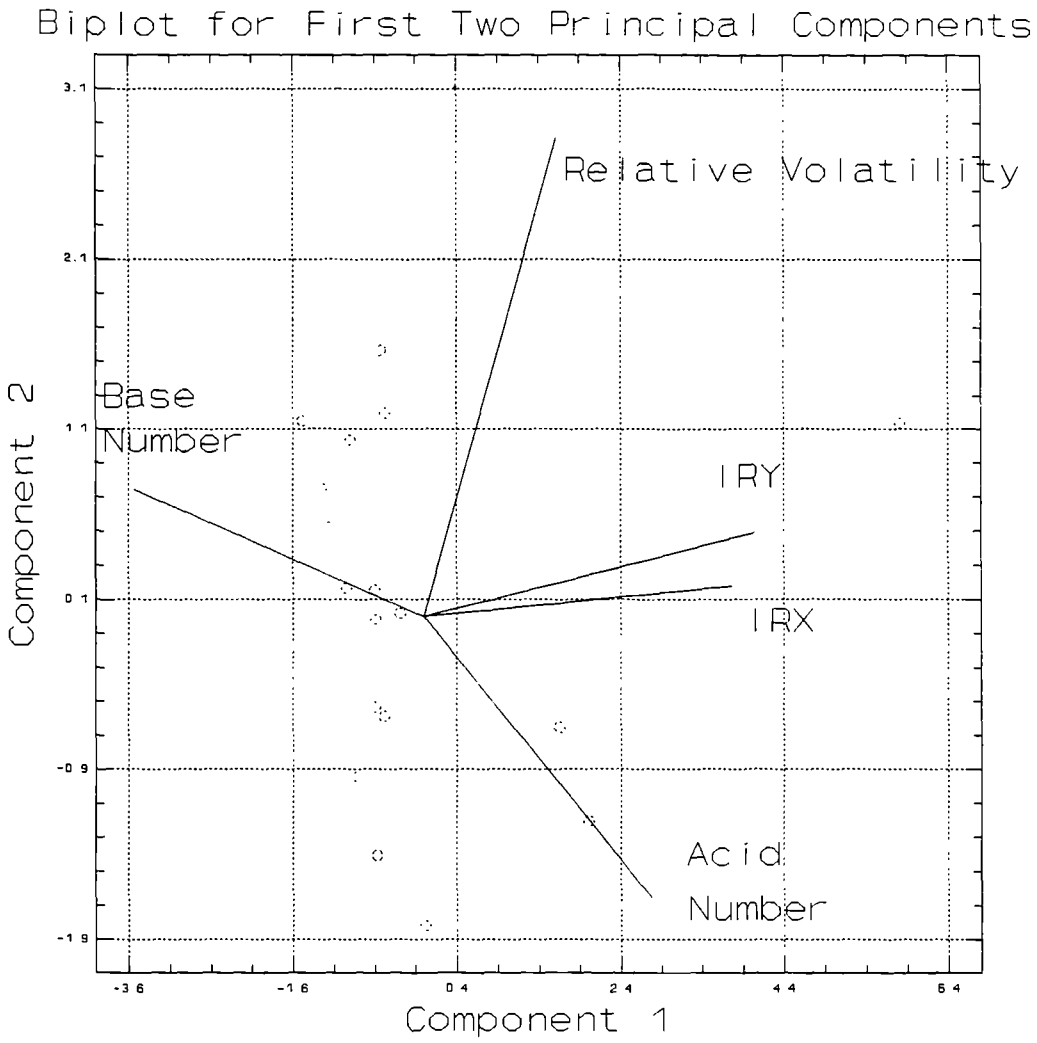


Figure 6.c

The five lines that intersect at (0,0) represent the original variables. The length of each vector is proportional to its contribution to the Principal Components. It reflects how each variable weights the two components. The angle between any two components is inversely proportional to the correlation between them. The biplot combines the information given by both the component weight and scatter plots.

Using the complete dataset it is obvious that sample ETHNO6 heavily influences the Principal Component Analysis. If more data had been collected the area around point 6 (ETHNO6) on the scatterplot would no doubt represent the extensively degraded oils from an engine test. The Principal Component Analysis method was repeated without this sample in the dataset.
The results from the analysis are given below;

Principal Components Analysis

Component Number	Percent of Variance	Cumulative Percentage
1	55.2	55.2
2	24.9	80.1
3	12.7	92.8
4	5.5	98.3
5	1.7	100.0

The first two Principal Components represent 80 percent of the total variability. The biplot of these first two components is given in Figure 6.d which shows that the data points are more scattered than in the previous example. The Principal Component equations are given below.

Principal Component 1 (PC1) = 0.474 (IRX) + 0.514 (IRY) - 0.260 (Relative volatility) - 0.523 (Base No) + 0.414 (Acid No)

Principal Component 2 (PC2) = - 0.405 (IRX) + 0.387 (IRY) + 0.766 (Relative volatility) - 0.305 (Base No) + 0.078 (Acid No)

The variables IRX, IRY and Acid No positively weight Principal Component One whereas the variables Relative volatility and Base No negatively weight Principal Component One. Principal Component Two is positively weighted by IRY, Relative volatility and Acid No, and negatively weighted by IRX and Base No.

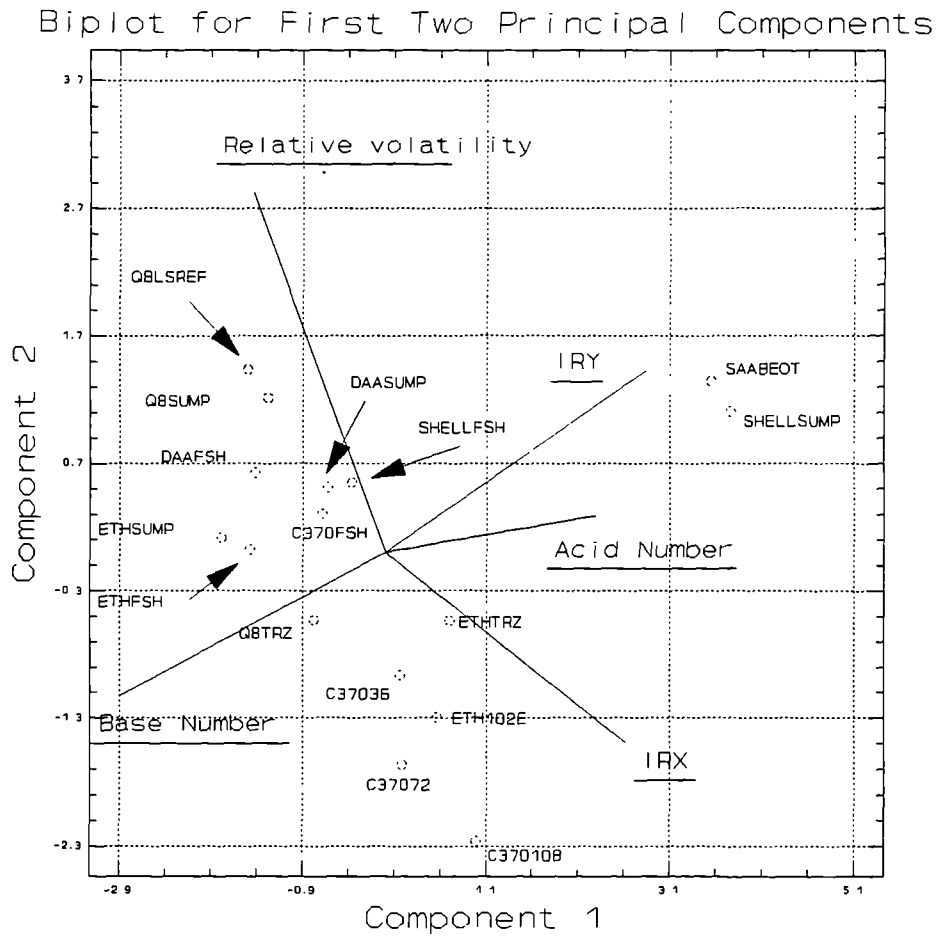


Figure 6.d

The vectors are therefore different to those shown in the first Principal Component Analysis. In the first analysis PC1 was positively influenced by all the variables except Base No, whereas in the second analysis PC1 is negatively influenced by both Base No and Relative volatility. The difference is observed in the spread of data points along PC1. The length of the Acid No vector, which is proportional to its contribution to the Principal Components, shows that this variable is the least significant. PC2 was heavily weighted by the variable Acid No in the first analysis and not in the second. Examination of the biplot shows that;

1) The first two Principal Components calculated for samples SAABEOT and SHELLSUMP indicate that they differ significantly from the other samples. The results from the analyses of these samples indicated a low Base Number, high Acid Number and oxidation (as determined by infra-red spectroscopy). The relative volatility experiments indicated fuel dilution for these samples.

2) The points representing the top ring zone samples are closer together on the biplot than on the first biplot because Acid No was weighted more in the first analysis.

3) Both PC1 and PC2 vary for the set of oil samples collected from the Petter W1 engine at 36 hour intervals.

As discussed in Chapter 3 the Acid Number results were obtained using a non-standard method which requires further development. The reliability of the method is yet to be proven and therefore the results must not be treated as absolute. As the Acid Number results were speculative and least influenced the above analysis the Principal Component Analysis was repeated without this variable. The results are given below;

Principal Components Analysis

Component Number	Percent of Variance	Cumulative Percentage
1	59.902	59.902
2	31.030	90.931
3	6.894	97.826
4	2.174	100.000

Using the four variables IRX, IRY, Relative volatility and Base No, 60 percent of the variation in the data is explained by the first Principal Component. The first two components describe 91 percent of the total variability, 10 percent more than the previous two examples.

The Principal Component equations are given below;

Principal Component 1 (PC1) = 0.531 (IRX) + 0.555 (IRY) - 0.296 (Relative volatility) - 0.568 (Base No)

Principal Component 2 (PC2) = - 0.376 (IRX) + 0.418 (IRY) + 0.755 (Relative volatility) - 0.337 (Base No)

These equations are very similar to those obtained previously, except that Acid No is not included. The biplot is shown in Figure 6.e, almost identical to the previous plot, Figure 6.d. One subtle difference between this plot and the previous one is that the points representing the two top ring zone samples now appear close to each other, as would be expected. Comparison of the two Acid Numbers for these samples explain the difference. Their position also indicates that they are significantly different from the corresponding fresh samples due to their relative volatilities alone. There is no indication of extreme oxidation as suggested by previous workers.

It is possible to repeat the Principal Component Analysis trying different combinations of variables, or by removing other samples from the dataset. This was considered to be unnecessary based on the last result, which was found to be an excellent way to compare the results obtained from the analyses of the fresh and used oil samples. Ideally more data is required, particularly with respect to top ring zone samples.

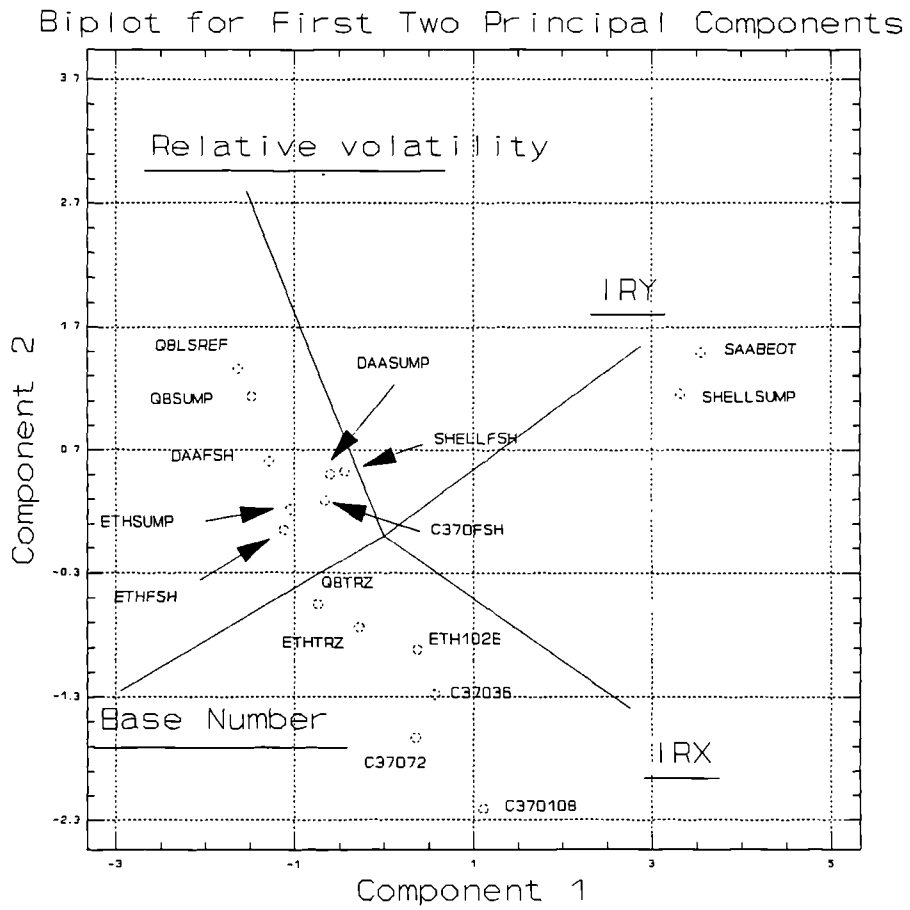


Figure 6.e

6.4 Conclusion

The interpretation of data obtained from a variety of analyses can be difficult if more than two, or possibly three, parameters are to be compared simultaneously. A multivariant statistical method known as Principal Component Analysis has been successfully applied to evaluate the fresh and used lubricating oils studied in this work. The top ring zone samples were found to be unique due to their low volatility and apparent lack of oxidation. To assess the full potential of top ring zone sampling considerably more data than is currently available would be required.

Considering the regions bounded by the vectors in Figure 6.e, the region

between those labelled IRX and IRY includes SAABEOT and SHELLSUMP. Both samples were subjected to fuel dilution and no longer suitable for engine lubrication. The region bounded by Relative Volatility and IRY includes none of the samples analysed in this work. Since the IRY component is probably due to nitration which only occurs when operating engines at high temperatures, it is likely that any volatile components within an oil will be vaporised, thus making it unlikely that any sample would show high levels of nitration combined with high volatility. All the new samples and most of the used oils which were still serviceable lie in the quadrant defined by Base Number and Relative Volatility. The quadrant bounded by Base Number and IRX includes most of the samples from engine tests where the oil had deteriorated significantly and was probably not fit for further use.

Whilst many more samples would need to be considered before definite conclusions could be made this preliminary study suggests that monitoring the four functions may provide a satisfactory screening technique for assessing whether or not oils are suitable for continued use in an engine.

The application of PCA to compare fresh and used oils, including top ring zone samples, based on a range of analyses, has not previously been investigated in these laboratories. The method should be further developed with a much wider range of samples.

CHAPTER 7 Review

The work in this thesis has shown the importance of volatility characteristics in the analysis of used oils. In Chapter 2 the relative volatility results, which correlate directly with Noack results, showed that the relative volatility of an oil decreases as its service life increases. The samples taken from a Petter W1 at 36 hour intervals gave the following results.

Time in engine/hours	Relative volatility	% decrease
0	1.049	00.0
36	0.831	20.8
72	0.710	32.3
108	0.613	41.6

The % decrease in relative volatility was calculated by using the following;

$$\%\ decrease = relative\ volatility \frac{(\ fresh\ -\ used\ )}{fresh} \times 100$$

A maximum of 41.6% was observed for the decrease in relative volatility, after the oil had been operating for 108 hours in a Petter W1.

Samples which show decreased volatility are likely to have been subjected to one or more of the following;

1. Evaporative losses
2. Oil oxidation
3. Soot contamination

If the loss in volatility was due to oxidation of components within the oil then

comparisons made between fresh and used oils are valid. However, if evaporative losses are significant then comparisons become more complex due to concentration effects. Wooton et al [29] discussed the presence of dispersants which have carbonyl functions. They indicated that the concentration of the dispersant can be cancelled out providing its concentration remains constant (by subtracting the fresh oil from the used oil IR spectrum). The possibility of the additive dropping out from the oil with the soot during engine oil filtration was mentioned. The problem was sometimes eliminated by looking further into the infrared spectrum. If the C-O-C absorbance, produced by ethers and esters, showed a similar profile to that of the C=O absorbance then they deduced that the dispersant had not dropped out. Other species however absorb in the C-O-C region, for example sulphate species, which can further complicate the interpretation of the spectra. Although mentioning the problem of the dispersant absorbing in the same region as oxidation products, Wooton et al did not discuss the possibility of additive concentration due to evaporative loss.

The results in Chapter 2 also showed that degraded gasoline oils can contain significant amounts of high volatile material, assumed to be fuel contamination. The shearing of polymers could also lead to the production of low molecular weight components, although probably not to the degree suggested by the thermogravimetric results. Fuel dilution was discussed by Coates and Setti [26] where loss of ZDDP was observed as a result of a volumetric displacement of lubricant components by the added fuel. Again there was no mention of additive concentration, as opposed to additive dilution.

In Chapter 3 both Base and Acid Number determinations were described. The Base Number results, using IP 177 solvent, were similar for those oils taken from a Petter W1 at regular intervals. Assuming that loss of volatility is due to evaporative losses alone, a decrease in volatility would result in an increase in Base Number due to additive concentration. Since a 10% decrease in volatility results in an approximate 10% increase in Base Number, Base Number values

can be predicted with the further assumption that no degradation has occurred. The data below, in Table 7.a, shows the experimental results and predicted results for the Petter W1 samples. The difference between the experimental and predicted results therefore indicates the loss in Base Number due to degradation. These values are shown in Table 7.b. It is important to note that no corrections have been made for loss of volatility due to oil oxidation or particulate content.

Table 7.a

Time in engine/hours	% decrease in relative volatility	Experimental Base Number / mgKOH/g oil	Predicted Base Number / mgKOH/g oil
0	0	7.55	7.55
36	20.8	7.20	9.12
72	32.3	8.05	9.99
108	41.6	8.00	10.69

Table 7.b

Time in engine/hours	Predicted-Experimental Base Number Results / mgKOH/g oil
0	0
36	1.92
72	*1.94*
108	2.69

Similar calculations based on experimental results from the diesel oil samples, including top ring zone, were carried out to give the predicted Base Numbers

shown in Table 7.c. The differences between predicted and experimental results are given in Table 7.d.

Table 7.c

Oil Sample	% decrease in relative volatility	Experimental Base Number/ mgKOH/g oil	Predicted Base Number/ mgKOH/g oil
Q8LSREF	0	9.4	9.4
Q8TRZ	30.9	9.9	12.3
Q8SUMP	5.0	9.1	9.9
ETHFSH	0	9.4	9.4
ETHTRZ	24.5	8.55	11.7
ETHSUMP	0	8.75	9.4
DAAFSH	0	9.2	9.2
DAASUMP	16.7	7.1	10.7

Table 7.d

Oil Sample	Predicted-Experimental Base Number Results/ mgKOH/g oil
Q8LSREF	0
Q8TRZ	2.4
Q8SUMP	0.8
ETHFSH	0
ETHTRZ	3.2
ETHSUMP	0.7
DAAFSH	0
DAASUMP	3.6

The results indicate that if the relative volatility is taken into consideration a reduction in Base Number is observed for the used oils, particularly top ring zone oils. The degree of volatile loss is obviously important.

The Base Number results obtained for the fuel contaminated gasoline oils were very low. This suggests that either the fuel dilution has counteracted the effect of volatile losses or that acids in the fuel have neutralised the basic components present within the oil, or other chemical species have reacted with the basic components. Of these possibilities the most likely to be responsible for Base Number reduction is neutralisation of acid combustion by-products. A thermogravimetric method could be developed to determine both the extent of fuel dilution and volatility characteristics of used lubricating oils.

The Acid Number results were obtained using a back titration technique, where acid is added, to determine the Base Number, and then alkali is added to determine the Acid Number. The only significant results were obtained for the fuel diluted oil samples, which gave high Acid Number and low Base Number values. This shows that a minimum Base Number is reached before acidic components become significant. It should be noted that the back titration non-aqueous conductimetric method has not been fully developed, but appears to be a viable alternative to the potentiometric method. Preliminary studies of a new colour indicator method show encouraging results. The oil changes from yellow to bright purple. Measurements carried out so far essentially confirm the results obtained by conductimetric back titration. When carrying out Principal Component Analysis the Acid Number results had little influence in oil discrimination. For the vast majority of lubricating oil samples Base Number results seemed to be sufficient. Negative Acid Number values obtained for several samples, probably due to precipitation of additive components during titration. Further work involving alternative solvent systems is required before a general, reliable Acid Number determination method can be achieved.

Chapter 4 described the infrared spectra of the neat and separated oil samples. The analysis of the neat samples showed that the species that changed most rapidly occurred between 1800cm^{-1} and 1500cm^{-1} and these species are principally assigned to carbonyl compounds with nitrated species also towards the lower end of the range. The increase in intensity of this region was monitored by Coates and Setti [25] for a series of used oils by calculation of the integrated area under the spectral curve between 1880cm^{-1} and 1650cm^{-1}. They did not however make allowances for a change in oil volume due to, for example, fuel contamination or base oil loss. The IR spectra of neat samples analysed, in Chapter 4, showed that components within the fresh oils also showed absorption in this region of the spectrum, assigned to polyisobutenyl succinimide type dispersants (C=0), ester based viscosity index improvers (C=O) and aromatic species. The heavily contaminated diesel samples gave poor infrared spectra due to absorption and scattering of the infrared beam. With these problems in mind the oil samples were separated using dialysis. The method conveniently separated the high molecular weight components from the low molecular weight components. The dialysate fraction contained base oil, antioxidants and of particular interest the oxidation products. The residue contained the high molecular weight additives such as the dispersants, VII and detergents. Having shown that the repeatability of the technique was good the dialysates were examined in more detail. As mentioned above, the region which changed most rapidly was between 1800-1500cm^{-1}. Unlike Coates and Setti the spectral region was divided into two regions, 1780cm^{-1} - 1680cm^{-1} and 1635cm^{-1} - 1565cm^{-1}, named X and Y respectively. The increase in intensity of the two regions was calculated by integration of the area under the two curves. It is important to emphasise that in this work the degree of oxidation was determined from the infrared analysis of the dialysates and **not** the neat samples. The soot and other insolubles remained in the residue. There is a possibility therefore that oxidation products would remain attached to the particulates, although the dialysis procedure continually rinses the residue with fresh solvent over a period of 6 hours. The particulates could also block the membrane pores, slowing down the

dialysis. If the degree of oxidation was high then it is quite likely that high molecular weight oxidation products would remain in the residue, resulting from polymerisation reactions. The infrared analysis of the dialysates was very straight forward, as the problems associated with the analysis of the neat samples were eliminated. Any increase in absorption in region X or Y must be due to degradation-type components or low molecular weight contaminants such as fuel. The integral regions would be slightly overestimated if the oxidation products were concentrated by the loss of base oil.

This technique has not been previously described for the analysis of used oils and has proved extremely useful for the analysis of top ring zone oil samples. From the measurements of the integral regions the top ring zone samples did not show significant oxidation. Oil which indicated a significant degree of oxidation, based on region X, were those obtained from industrial engine tests and from vehicles in service. An increase in intensity was observed in the spectral region Y for those oils which were contaminated with fuel. The information gained from the oil samples analysed was of great interest and warrants the continuation of further work on a larger range of oil samples in the future.

Another method of separation was attempted based on liquid phase chromatography. The polar components adsorbed strongly onto the solid phase silica gel, whilst the non-polar components were eluted with pentane, the mobile phase. Recovery of the polar fraction proved to be difficult, which discouraged the use of this method. It was also thought that several of the additives would alter in composition, for example an over-based sulphonate could lose the calcium carbonate component. As the dialysis separation was successful the separation by liquid chromatography was not pursued.

The Four-Ball Tester, as described in Chapter 5, was modified to enable the analysis of top ring zone samples. The volume required to run one test was reduced from 8ml to 1½ml. To determine the initial seizure load and weld load a

minimum of 9ml was required, which allowed for 6 experimental runs on each sample.

The end of test oil taken from a SAAB engine test had a low initial seizure load, 67kg, which was thought to be due to the fuel contamination, as observed in the thermogravimetric result. This explanation was also thought to apply to the gasoline top ring zone sample, which was known to have a degree of fuel dilution. The remaining fully formulated oils, except the fully synthetic oil, showed similar initial seizure load results, 112kg, including the oil sample from a Petter W1 after 108 hours and the top ring zone sample from the Petter AA1. The result obtained for the low viscosity base oil showed that it was unable to support a thin film at a load of 56kg. The fully synthetic oil supported a thin film up to a load of 160kg, which was significantly higher than other results. The weld load results were very similar for all the oils tested, except those obtained from the pure base oils, which had poor high load characteristics.

The comparison of results obtained from used oil samples using the techniques described in Chapter 5, was thought to be of little use without complimentary information regarding the degree of fuel dilution, soot/particulate content, volatility characteristics and viscosity.

Chapter 6 described the application of Principal Component Analysis to the interpretation of results obtained from a range of oil samples using a variety of techniques. The data collected from the analyses included relative volatility, Base Number, Acid Number and infra-red spectral data in the wavenumber range $1500cm^{-1}$-$1800cm^{-1}$. The software package used to manipulate the data, Statgraphics, generates linear combinations of the variables called principal components. The principal components describe the variability within the data. The first two principal components usually account for most of the variability in the data and can be plotted against one another to give a scatterplot. Each point on the scatterplot represents one oil, the co-ordinate of which is based on all the

variables chosen. Different areas on the scatterplot represent different types of oil, for example fuel contaminated severely degraded oils or fresh diesel oils. The location of a point, representing an oil, therefore shows the overall condition of the oil based on Base Number, infrared analysis etc. The application of Principal Component Analysis to the interpretation of data collected from the analyses of fresh and used oils, including top ring zone oil samples, had not been previously investigated in these laboratories. The method was found to be very useful, showing that top ring zone samples are quite unique due to their low volatility and apparent negligible oxidation.

The Principal Component Analysis technique could be applied to evaluate development oils. This could be accomplished by initially developing Principal Components based on results from fresh and used oils, where the performance of each oil was known to be poor, borderline or good. By plotting the first two Principal Components the oils should fall into three regions of poor, borderline and good performance. The suitability of any future oil could then be determined by analysing the fresh oil, followed by the analysis of the oil taken from an engine test and finally calculating the Principal Components previously attained for oils of known performance.

The work presented in this thesis has described the analyses of fresh and used oils using both new and extended methods. The volatility of the used oil samples, particularly top ring zone, has shown that the volatility characteristics must be determined when analysing oil samples. It has been shown that the results obtained from a range of analyses can be compared using the statistical method known as Principal Component Analysis.

CHAPTER 8 Summary and Further Work

8.1 Summary

Techniques have been developed for the specific analysis of oils sampled from the top ring zone of operating combustion engines. A range of fresh and used oils have been analysed, the results of which have been compared using a multivariant statistical method known as Principal Component Analysis.

A Four Ball Tester has been successfully modified to reduce the amount of oil sample required. The initial seizure load and weld load can be determined from as little as 9ml of sample, resulting in the examination of top ring zone samples. The results obtained from a range of both fresh and used automotive oils indicated that this method alone was not suitable to differentiate between a range of oil samples. The top ring zone oil samples, using this technique, were similar in character to fresh oils.

A unique thermogravimetric method for the determination of volatility was developed, based on work carried out for the Institute of Petroleum Thermal Analysis Panel. Using squalane as a standard, relative volatility results were determined, requiring only 4mg of sample. Results from a range of samples of known Noack values showed that there was a linear correlation between relative volatility results and Noack results. The method was successful for both fresh and used oils which had not been contaminated with fuel. The relative volatility results indicated that the diesel top ring zone samples were similar in character to those obtained from industrial engine tests.

The determination of Base Number by non-aqueous conductimetric titration was found to be an excellent method for analysing both fresh and used oil samples. Work carried out for the Institute of Petroleum confirmed the repeatability of the method. An inter-laboratory program has confirmed the reproduibility of this method. The results obtained from the used oils, particularly of low volatility, were

higher than expected due to concentration effects. The Acid Numbers were obtained for the oil samples using a back titration conductimetric technique, but the method was not fully satisfactory. Results obtained for one oil however suggested that an acid base colour indicator might provide an alternative method for Acid Number determinations.

The infrared analyses of the neat samples showed that interpretation of the spectra can be difficult due to the many additives present within a fully formulated oil and contaminants such as soot. Dialysis of the samples was found to be a promising technique for isolating the oxidation products from the high molecular weight additives and particulates. The dialysate contained the oxidation products, base oil and antioxidants. The degree of oxidation was determined from the infra-red analysis of the dialysate of the oil samples. The infra-red spectra derived from top ring zone samples were not found to show signs of significant carbonyl oxidation.

A technique known as Principal Component Analysis was used to interpret the results obtained from the analyses of the oil samples. The technique very successfully compares the oil samples based on all the results obtained from the various analyses. The top ring zone samples analysed were unique due to their very low volatility and lack of oxidation, compared with oil samples obtained from genuine engine tests.

8.2 Further Work

Before top ring zone samples can be fully characterised there are many engineering problems which must be overcome. Sufficient samples are required over a sustained period of engine operation. When the samples are reliably obtained the analytical techniques described in this thesis will enable the degradation of an oil to be fully staisfactorily monitored.

The thermogravimetric method was not found to be suitable for samples contaminated with fuel. Another method could therefore be developed which would measure both the fuel content and relative volatility. The method could even be extended to measure the total insoluble content, based on present thermogravimetric methods.

The back titration Acid Number determination requires further development to assess the repeatability and reproducibility of the method. A range of standards are therefore required of known Acid Numbers, together with the support of the oil industry. A different method, based on a colour indicator titration, could be a far simpler alternative to the present methods available.

The use of Principal Components is a valuable technique which could be applied to the development of new oil formulations, using data obtained from the analyses of the fresh and used oils.

8.3 Achievements

Additional techniques have been developed for the characterisation of top ring zone samples, the overall aim of the work. The four objectives have been accomplished, including;

1. Modification of Four Ball Tester
2. Development of method to determine volatility using thermogravimetry
3. Separation of oil samples by dialysis
4. Application of Principal Component Analysis

Unfortunately the number of top ring zone samples analysed were limited, due to problems encountered with the engines.

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